Supporting Information:

α-Diimine Synthesis via Titanium-Mediated Multicomponent Diimination of Alkynes with *C*-Nitrosos

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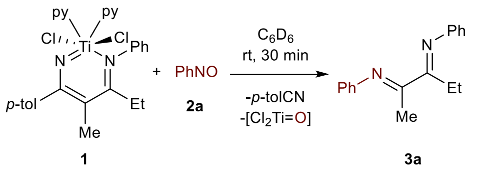
General Considerations

All air- and moisture-sensitive reactions were carried out in a nitrogen-filled glovebox (MBRAUN) unless otherwise specified. Standard solvents for air- and moisture-sensitive reactions were either deoxygenated by sparging with Ar and dried by passing through activated alumina columns of a Pure Process Technology solvent purification system (benzene, ether, pentane, hexanes, THF, toluene, CH_2Cl_2) or vacuum transferred from Na/Ph_2CO (C_6D_6) or CaH_2 (C_6H_5Br, C_6D_5Br, $CDCl_3$). C_6D_5Br was synthesized following literature procedure,[1] degassed, dried over CaH_2, and filtered through basic alumina prior to use. $[py_2TiCl_2(NPh)]_2$,[2] $[py_2TiCl_2(N\textit{p}\text{-tol})]_2$,[3] and $py_2TiCl_2ADA^{Et}$ (**1**),[4] and were synthesized according to literature procedures. Nitrosobenzene (**2a**), 2-nitrosotoluene (**2k**), N,N-dimethyl-4-nitrosoaniline (**2i**), and 2-methyl-2-nitrosopropane dimer (**2o**) were purchased from Sigma Aldrich. Other nitrosoarenes were synthesized by oxidation of their corresponding aniline using either Oxone® (**2b, 2d-g, 2j**) or $Na_2WO_4{\cdot}2H_2O/H_2O_2$ (**2c, 2h, 2l**) by adaptation of established literature procedures.[5-7] 1-nitrosoadamantane **2n** was prepared with mCPBA according to literature procedure.[8] 2-nitrosopyridine **2m** was synthesized according to established procedures.[9] Liquid alkynes and nitriles were freeze-pump-thaw degassed three times and passed through activated basic alumina prior to use. All other reagents were put under vacuum overnight prior to use or otherwise used as purchased. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance III HD 400 and 500 MHz spectrometers. Chemical shifts were referenced to the residual protio-solvent impurity for ^1H (s, 7.16 ppm for C_6D_5H; s, 7.26 for $CHCl_3$; s, 7.30 ppm, 7.02 ppm and 6.94 ppm for C_6D_4HBr)[7] and solvent carbons for ^{13}C (t, 128.06 ppm for C_6D_6; t, 77.2 ppm for $CDCl_3$). ^{19}F NMR spectra were referenced using an internal capillary of trifluoroacetic acid (neat), $F_3CC(O)OH$ ($\delta = -78.70$ ppm). Quantitative ^1H NMRs were taken with a 1,3,5-trimethoxybenzene internal standard (acquisition time = 5 s, delay time = 30 s, dummy scans = 0, number of scans = 8). Qualitative GC-MS spectra were recorded on an Agilent GC6890N-MSD5975 gas chromatograph-mass spectrometer fitted with a 7683 autosampler. A HD-5 column (5% diphenyl siloxane in the polymer) was used in the gas chromatograph and electron ionization technique was used for mass spectrometry detection. GC-FID chromatographs were collected on an Agilent 7890B GC system equipped with an HP-5 column (30 m, 0.32 mm, 0.25 μm, 7 in cage), an oxidation-methanation reactor (Polyarc® System, Activated Research Company) and an FID detector for quantitative carbon detection. High-resolution electrospray mass spectrometry (ESI-MS) was performed on all isolated samples using a Bruker BioTOF II ESI/TOF-MS with PEG 300 as an internal mass standard.

Addition of nitrosobenzene to **1** (NMR scale)



In situ Procedure: Diazatitanacyclohexadiene **1** (19.6 mg, 0.035 mmol) and internal standard 1,3,5-trimethoxybenzene (TMB) (4.0 mg, 0.024 mmol) were added to an NMR tube and dissolved in 0.5 mL C_6D_6, then nitrosobenzene (**2a**) (3.9 mg, 0.036 mmol, 1 equiv.) was added. A ^{1}H NMR spectrum was recorded after 30 min. Diimine **3a** was observed to have formed in an 81% yield, with 1:1 p-tolunitrile formation.

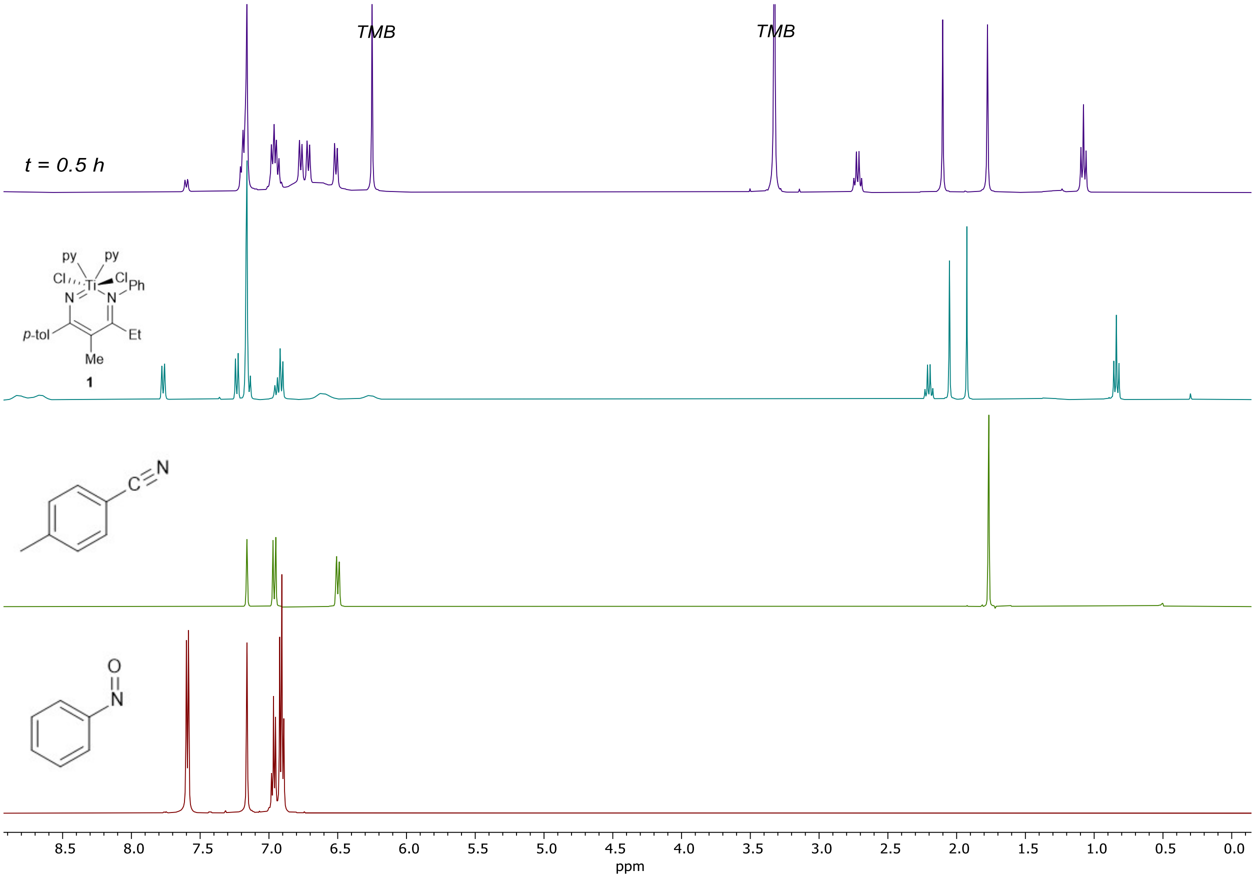


Figure S1. Stacked ^{1}H NMR spectra (C_6D_6) of nitrosobenzene addition to **1**; Bottom (red trace): nitrosobenzene (**2a**) prior to addition; Middle-bottom (green trace): *p*-tolunitrile, Middle-top (blue trace): **1** prior to addition of nitrosobenzene; Top (purple trace): After addition of nitrosobenzene to **1**, t = 0.5 h at room temperature, showing 81% yield of **3a** according to 1,3,5-trimethoxybenzene standard.

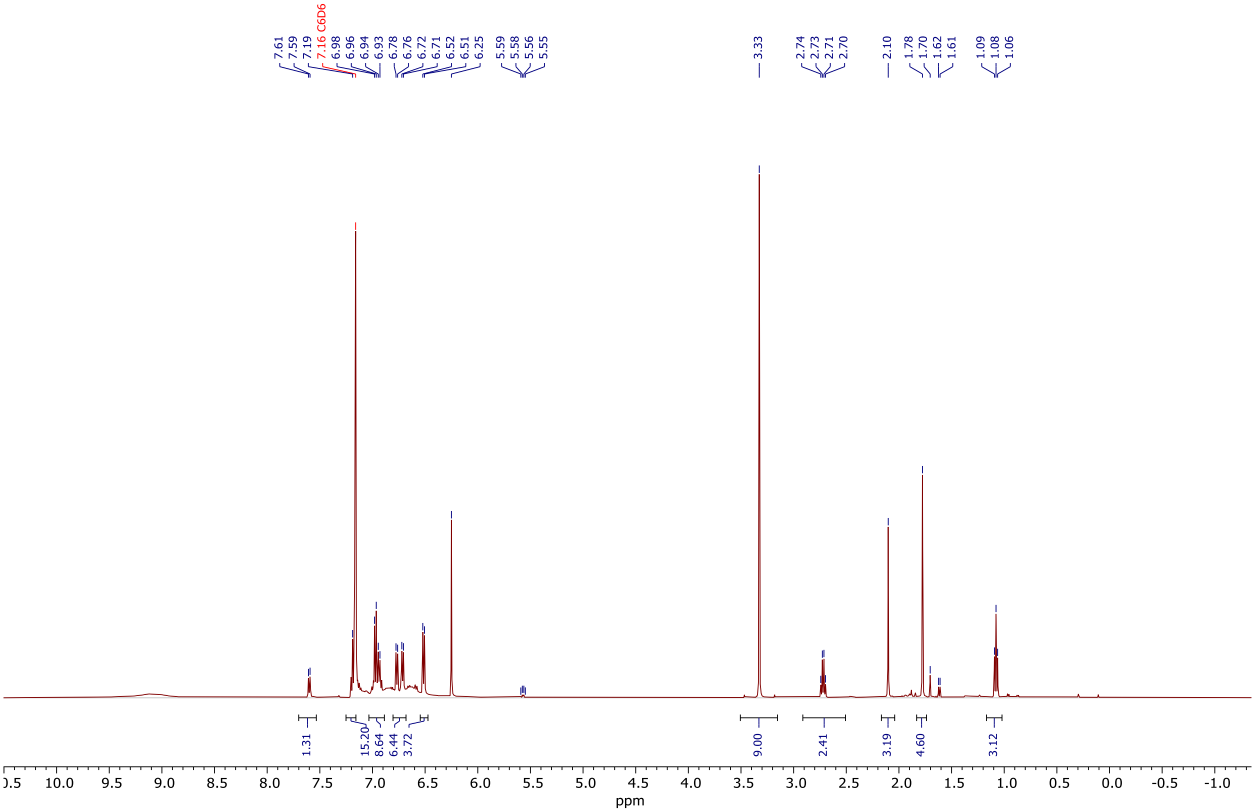
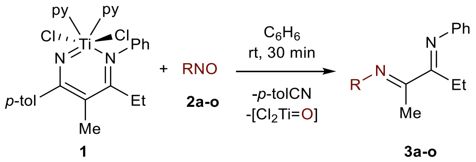


Figure S2. ^{1}H NMR spectrum (C_6D_6) after nitrosobenzene addition to **1** after 0.5 h, showing 81% yield of **3a** according to 1,3,5-trimethoxybenzene standard.

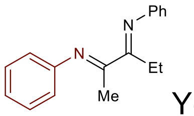
Scope of nitroso addition to py$_2$TiCl$_2$(ADA^{Et}) (**1**) (Table 1, **3a – 3o**) (isolation scale)



General procedure: py$_2$TiCl$_2$(ADA^{Et}) (**1**) (110.7 mg, 0.2 mmol, 1 equiv.) and nitrosobenzene (**2a**) (21.4 mg, 0.2 mmol, 1 equiv.) were added to a 20 mL scintillation vial with 3 mL of C_6H_6. The reaction was stirred for 0.5 hours at room temperature. The dark yellow-brown mixture turned an opaque orange with visible white solid. The reaction was quenched by the addition of saturated Na_2CO_3 (aq). The layers were separated, and the aqueous layer was extracted with hexanes. The organics were combined and dried over Na_2SO_4. After filtration, the volatiles (C_6H_6, hexanes) were reduced under vacuum. The removal of p-tolunitrile was achieved by heating at 35 °C under vacuum for 4 hours to afford 41.0 mg of pure **3a** in an 82% yield.

This procedure was repeated for **3b – 3o**. Diimines **3i** and **3m** were not able to be cleanly isolated, so NMR yields are instead reported (given below).

(2E,3E)-N^2,*N*^{3}-diphenylpentane-2,3-diimine (**3a**)



Yellow oil, 41.0 mg. 82% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.22 – 7.17 (m, 4H, CH(C*H*CH)$_2$CN), 6.94 (t, *J* = 7.5 Hz, 2H, C*H*(CHCH)$_2$CN), 6.77 (d, *J* = 7.8 Hz, 2H, CH(CHC*H*)$_2$CNCCH$_2$CH$_3$), 6.71 (d, *J* = 7.7 Hz, 2H, CH(CHC*H*)$_2$CNCCH$_3$), 2.72 (q, *J* = 7.5 Hz, 2H, CH$_3$C*H$_2$*), 2.10 (s, 3H, C*H$_3$*), 1.08 (t, *J* = 7.5 Hz, 3H, C*H$_3$*CH$_2$). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.71, 167.20, 151.62, 151.60, 129.29, 129.28, 124.00, 123.73, 119.13, 118.74, 22.04, 15.59, 13.27. **ESI-HRMS (m/z):** calcd. for $C_{17}H_{18}N_2Na^+$, 273.1368; found, 273.1368.

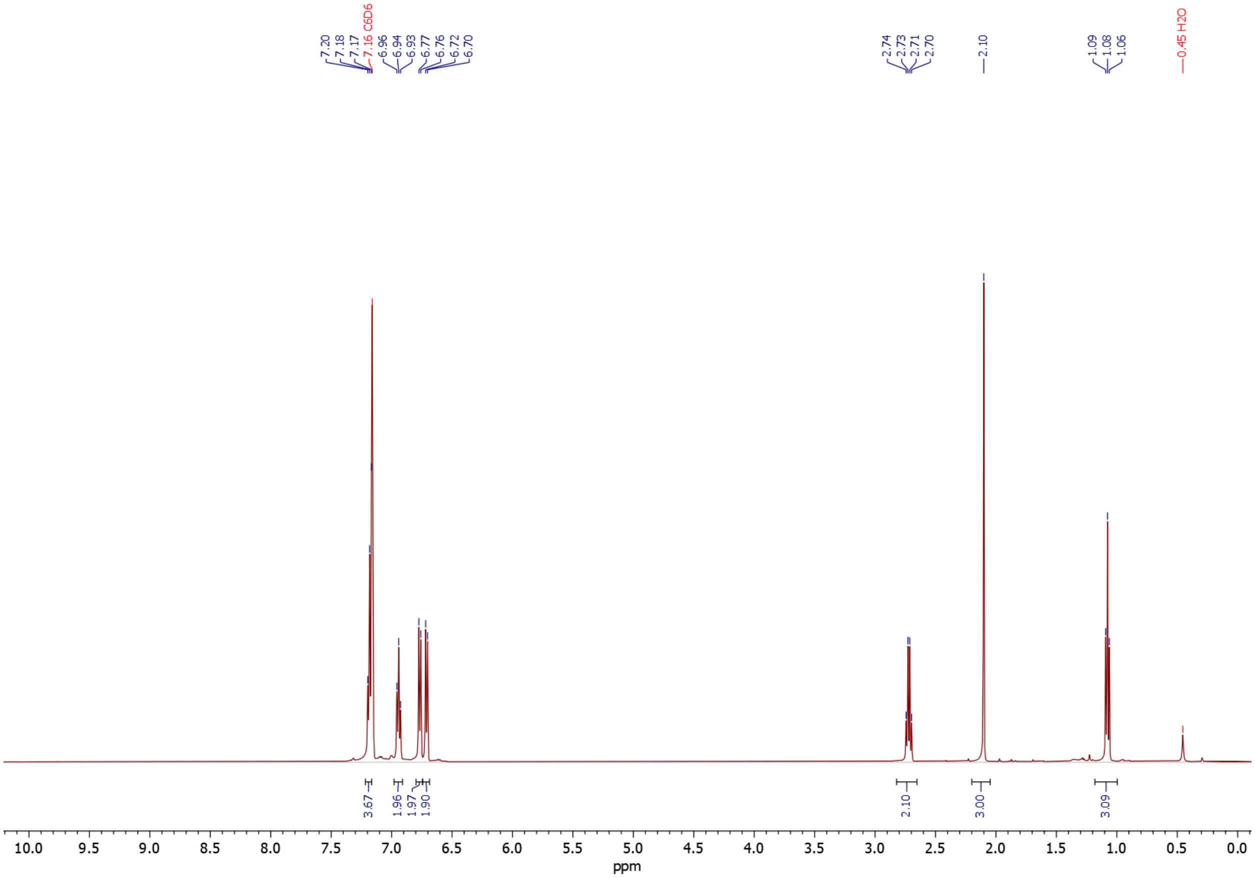


Figure S3. ^{1}H NMR spectrum of **3a** in C_6D_6.

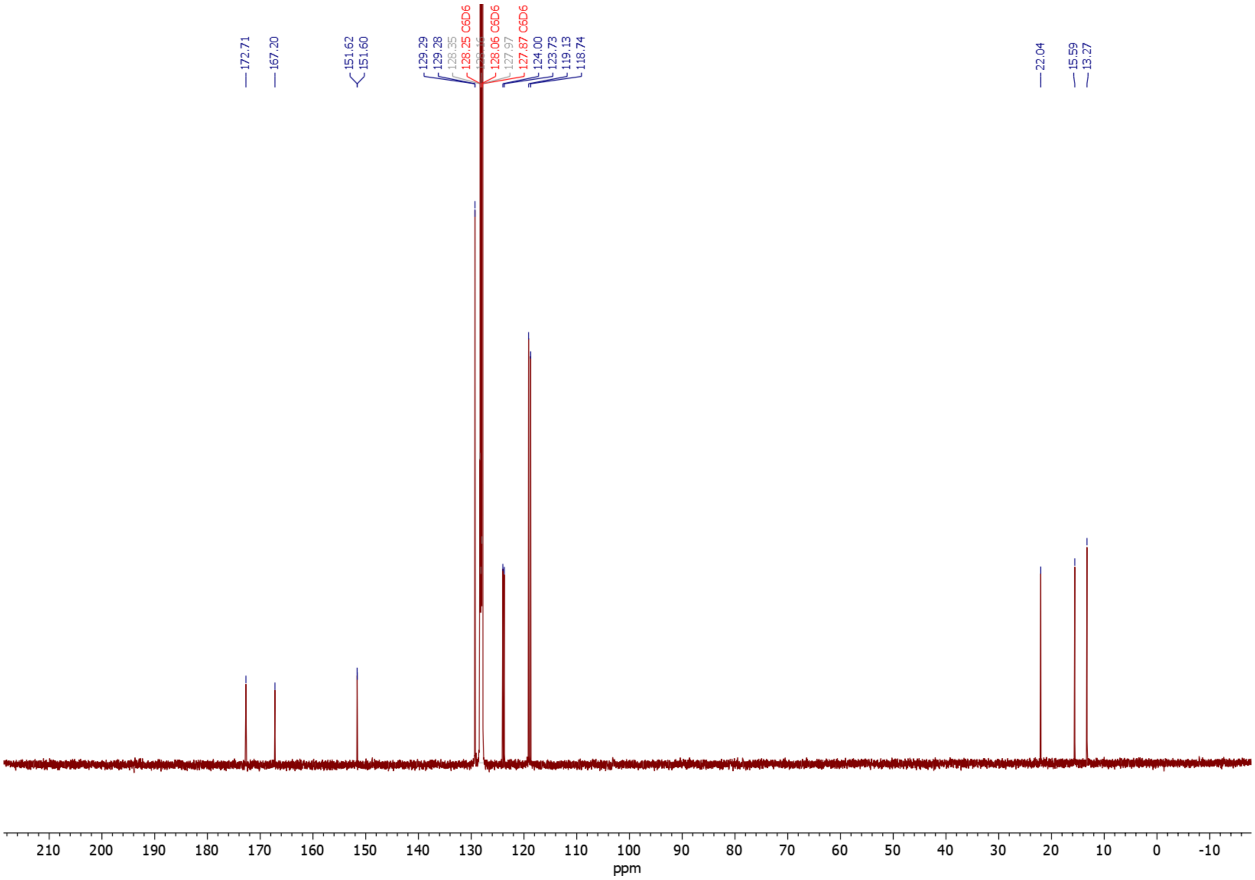


Figure S4. ^{13}C NMR spectrum of **3a** in C_6D_6.

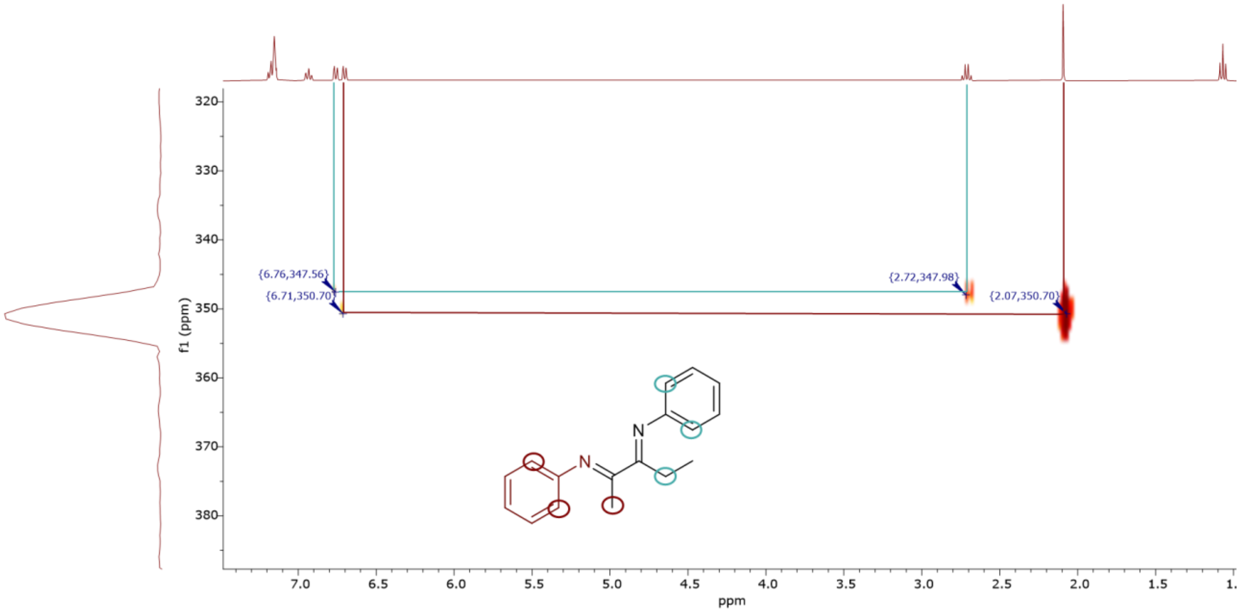
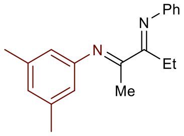


Figure S5. ^{1}H-^{15}N HMBC NMR spectrum of **3a** in C_6D_6.

(2E,3E)-*N*^{2}-(3,5-dimethylphenyl)-*N*^{3}-phenylpentane-2,3-diimine (**3b)**



Yellow oil, 42.8 mg. 77% isolated yield. **^{1}H NMR (500 MHz, C$_6$D$_6$)** δ 7.22 – 7.17 (m, 2H, CH(C*H*CH)$_2$CN), 6.95 (tt, *J* = 7.4, 1.2 Hz, 1H, C*H*(CHCH)$_2$CN), 6.79 (dd, *J* = 8.4, 1.2 Hz, 2H, CH(CHC*H*)$_2$CN), 6.63 (s, 1H, C*H*(CCH$_3$)$_2$(CH)$_2$C), 6.43 (s, 2H, CH(CCH$_3$)$_2$(C*H*)$_2$C), 2.76 (q, *J* = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 2.16 (s, 3H, C*H*$_3$), 2.16 (s, 6H, CH(CC*H*$_3$)$_2$(CH)$_2$C), 1.12 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C$_6$D$_6$)** δ 172.83, 166.83, 151.78, 151.72, 138.71, 129.30, 125.70, 123.70, 118.77, 116.81, 22.06, 21.41, 15.67, 13.34. **ESI-HRMS (m/z):** calcd. for C$_{19}$H$_{22}$N$_2$H$^+$, 279.1861; found, 279.1849 (diff. 0.0012).

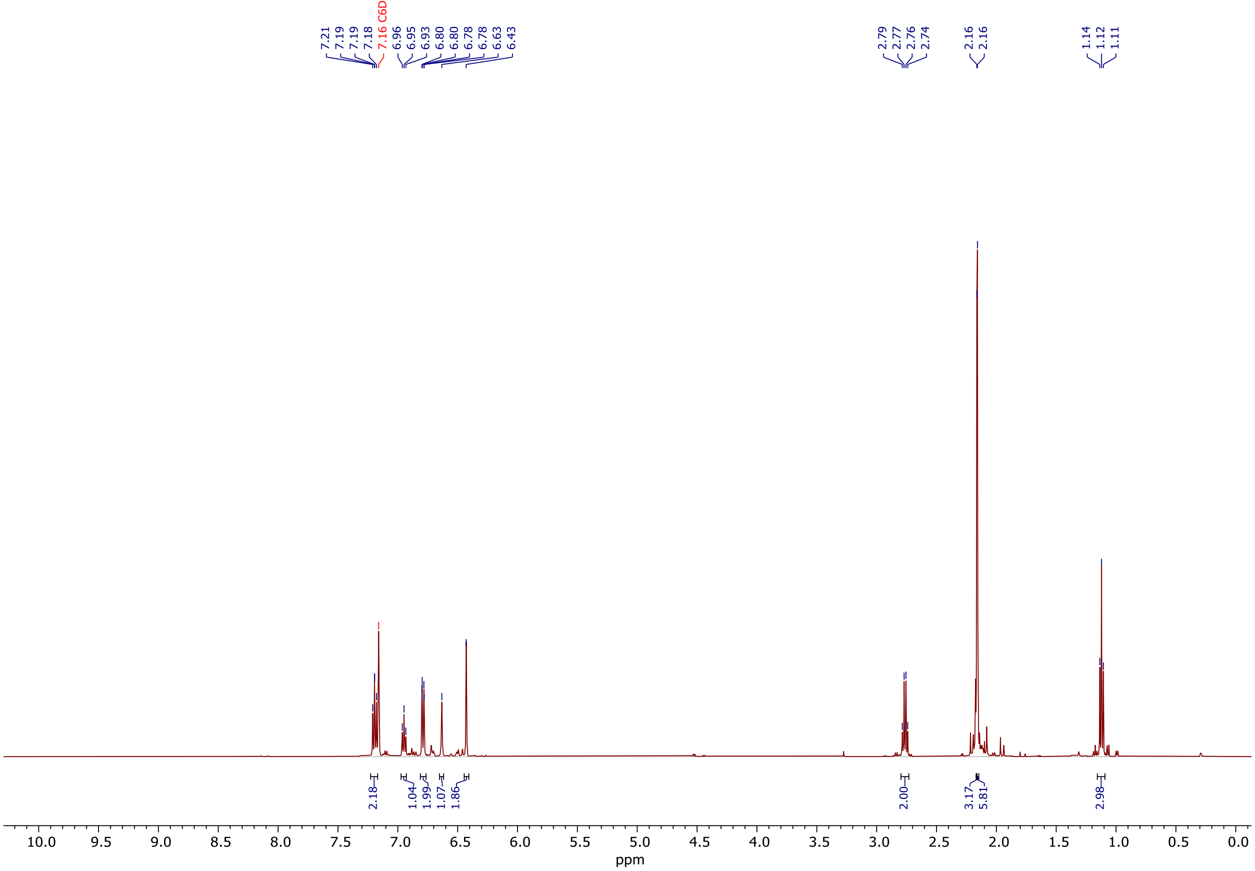


Figure S6. ^{1}H NMR spectrum of **3b** in C$_6$D$_6$.

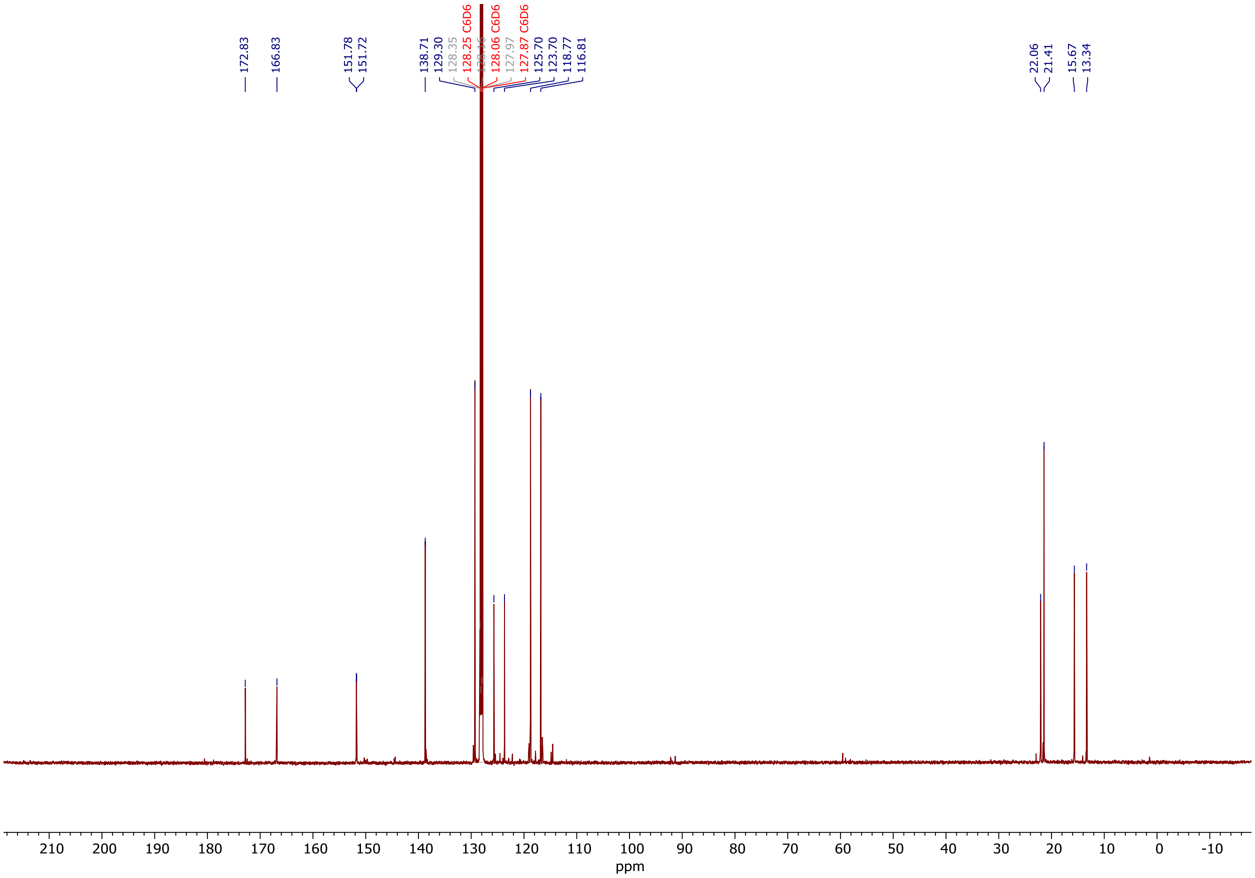
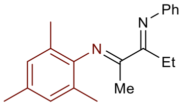


Figure S7. ^{13}C NMR spectrum of **3b** in C_6D_6.

(2E,3E)-N^2-mesityl-N^3-phenylpentane-2,3-diimine (**3c**)



Yellow oil, 44.1 mg. 76% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.20 – 7.17 (m, 2H, CH(C*H*CH)$_2$CN), 6.97 – 6.90 (m, 1H, C*H*(CHCH)$_2$CN), 6.83 (s, 2H, CH$_3$(C*H*CH$_3$)$_2$C), 6.77 (d, *J* = 7.8 Hz, 2H, CH(CHC*H*)$_2$CN), 2.80 (q, *J* = 7.5 Hz, 2H, C*H$_2$*CH$_3$), 2.22 (s, 3H, C*H$_3$*), 2.00 (s, 3H, C*H$_3$*(CHCH$_3$)$_2$C), 1.99 (s, 6H, CH$_3$(CHC*H$_3$*)$_2$C), 1.13 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H$_3$*). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.35, 167.83, 151.60, 146.90, 132.37, 129.27, 129.15, 124.53, 123.74, 118.85, 21.92, 20.86, 18.17, 15.91, 13.36. **ESI-HRMS (m/z):** calcd. for $C_{20}H_{24}N_2Na^+$, 315.1837; found, 315.1849 (diff. 0.0012).

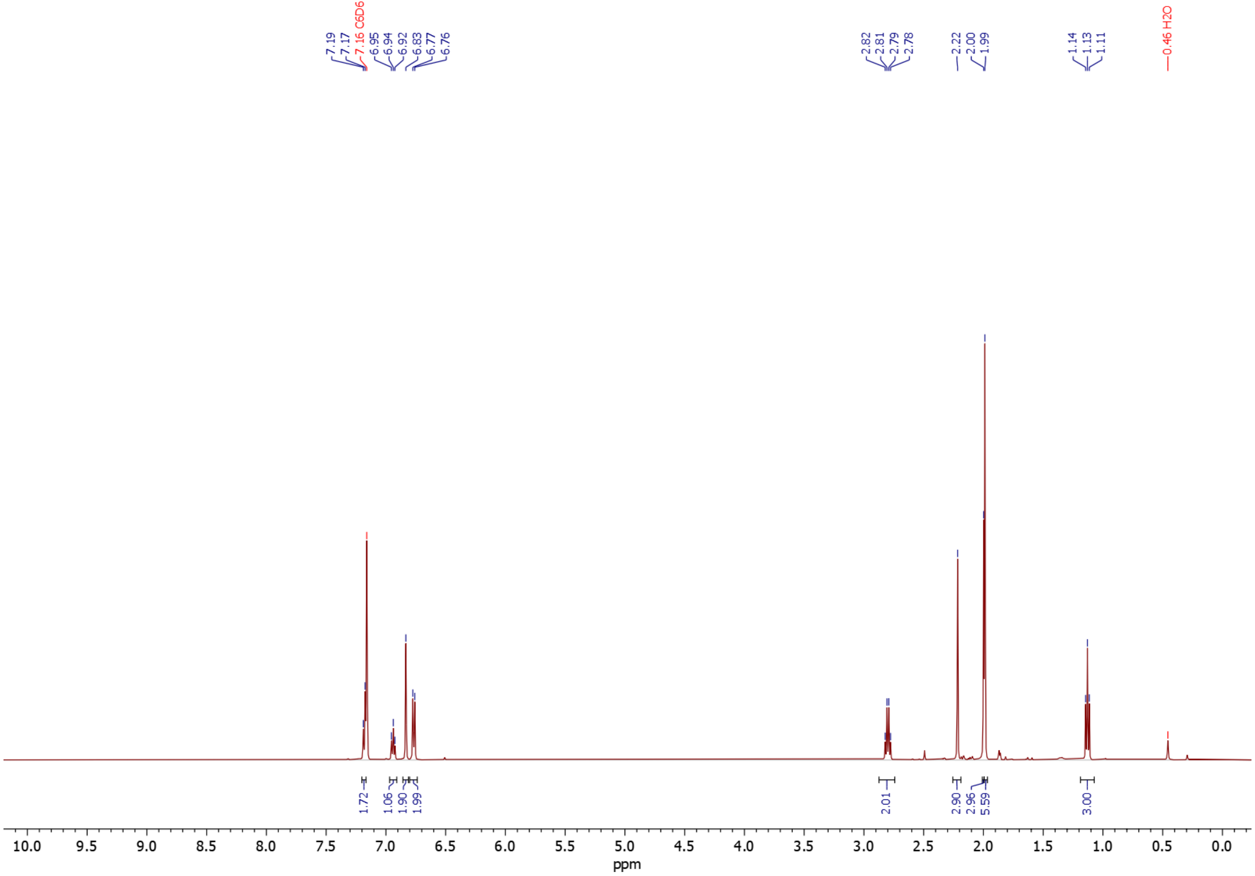


Figure S8. ^{1}H NMR spectrum of **3c** in C_6D_6.

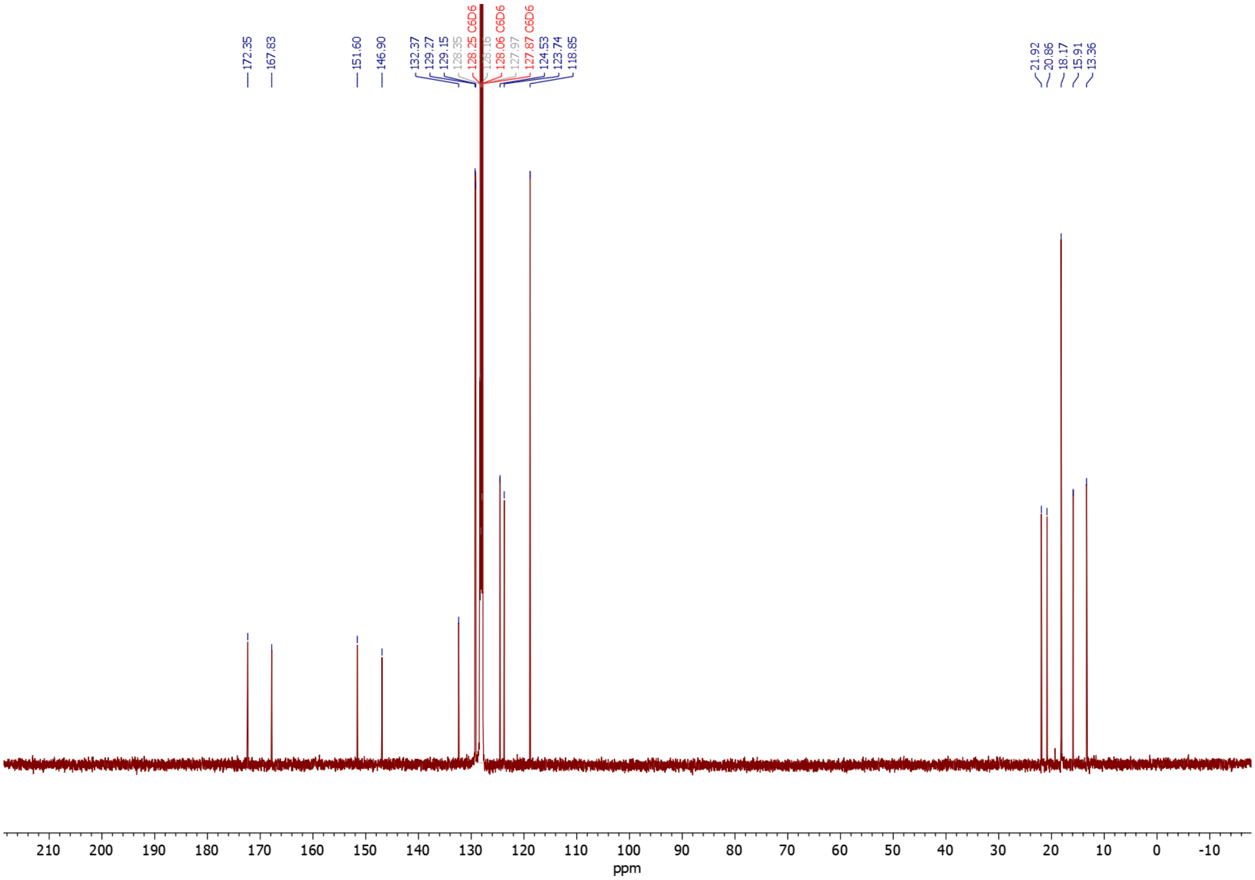
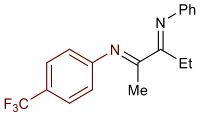


Figure S9. ^{13}C NMR spectrum of **3c** in C_6D_6.

(2E,3E)-*N*^{3}-phenyl-*N*^{2}-(4-(trifluoromethyl)phenyl)pentane-2,3-diimine (**3d**)



Light orange crystalline solid, 56.6 mg. 65% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.34 (d, *J* = 8.3 Hz, 2H, CF_3-C-(C*H*CH)$_2$C), 7.23 – 7.18 (m, 2H, CH(C*H*CH)$_2$CN), 6.96 (tt, *J* = 7.4, 1.3 Hz, 1H, C*H*(CHCH)$_2$CN), 6.77 (d, *J* = 8.4 Hz, 2H, CH(CHC*H*)$_2$CN), 6.43 (d, *J* = 8.2 Hz, 2H, CF_3-C-(CHC*H*)$_2$C), 2.64 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 1.92 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.15, 168.04, 154.44, 151.30, 129.38, 126.58 (q, *J* = 3.7 Hz), 126.01 (q, *J* = 32.5 Hz), 125.23 (q, *J* = 271.3 Hz), 118.97, 118.64, 21.96, 15.71, 13.17. **^{19}F NMR (471 MHz, C_6D_6)** δ -62.07 (vs. TFA (neat), δ -77.80) **ESI-HRMS (m/z):** calcd. for $C_{18}H_{17}F_3N_2Na^+$, 319.1422; found, 314.1401 (diff. 0.0021).

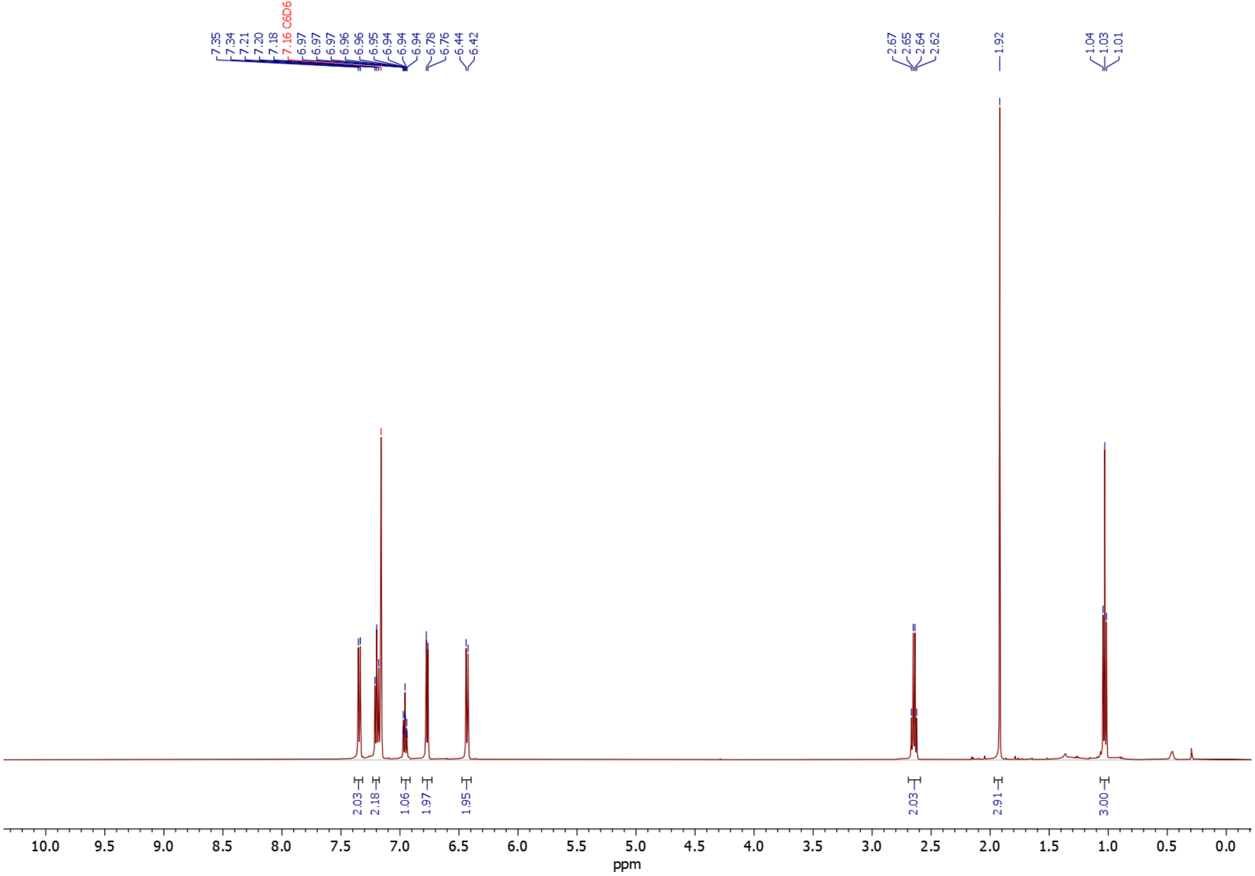


Figure S10. ^{1}H NMR spectrum of **3d** in C_6D_6.

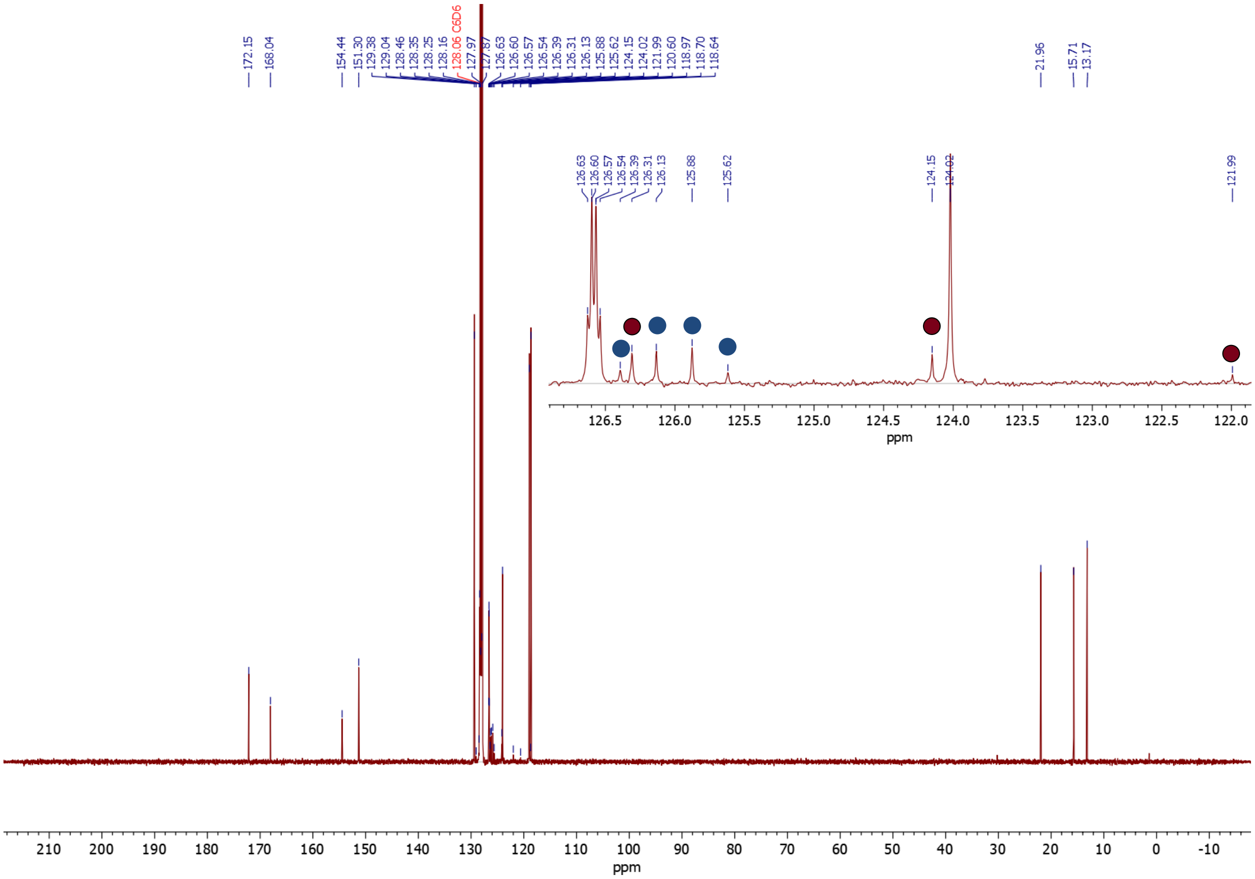


Figure S11. ^{13}C NMR spectrum of **3d** in C_6D_6, inset shows quartets from ^{13}C-^{19}F coupling.

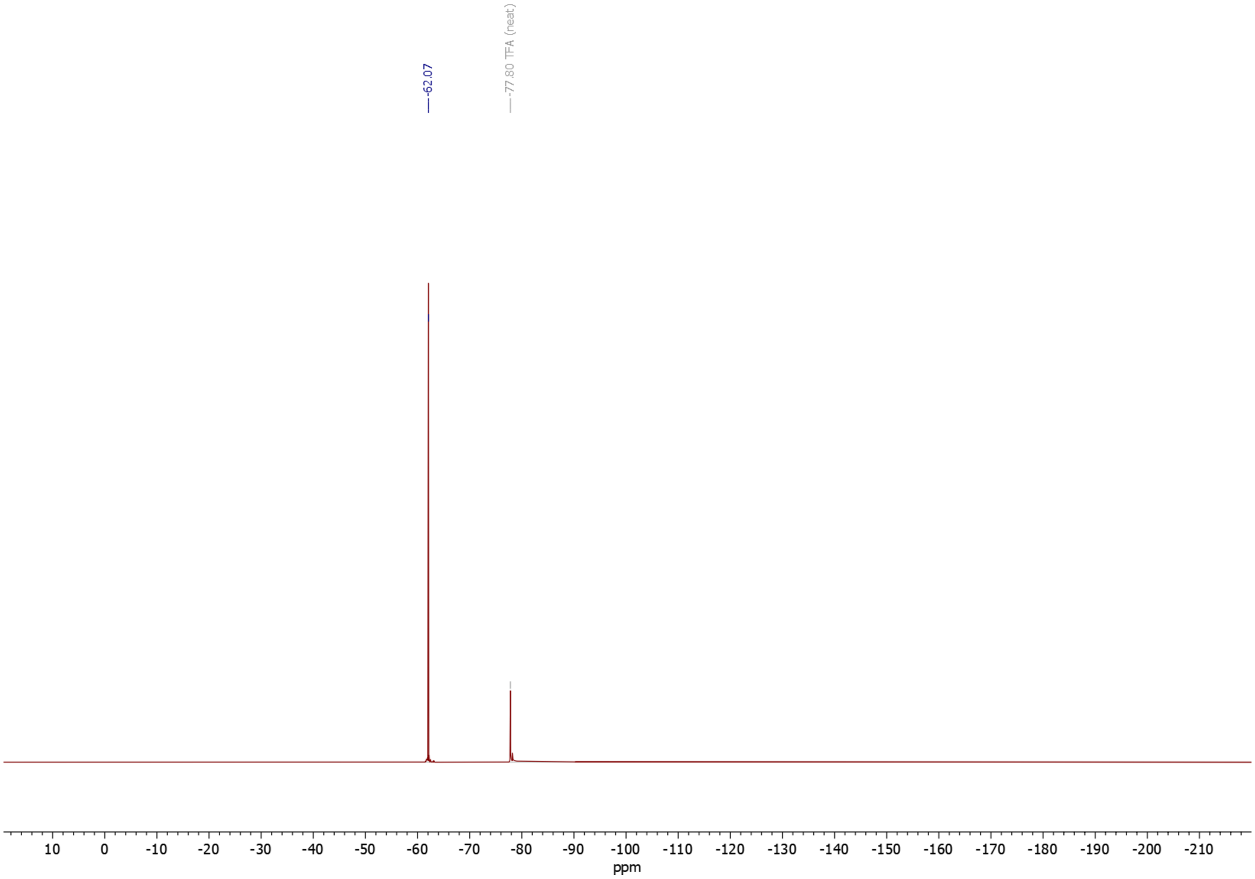
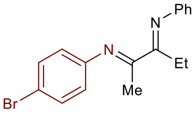


Figure S12. ^{19}F NMR spectrum of **3d** in C_6D_6 with trifluoroacetic acid (neat) reference capillary (δ -77.80).

(2E,3E)-*N*^{2}-(4-bromophenyl)-*N*^{3}-phenylpentane-2,3-diimine (**3e**)



Brown crystalline solid, 55.2 mg. 85% isolated yield. **^{1}H NMR (400 MHz, C_6D_6)** δ 7.23 (d, *J* = 8.5 Hz, Br-C-(C*H*CH)$_2$C), 7.21 – 7.16 (m, 2H, CH(C*H*CH)$_2$CN), 6.95 (t, *J* = 7.5 Hz, 1H, C*H*(CHCH)$_2$CN), 6.77 (d, *J* = 7.1 Hz, 2H, CH(CHC*H*)$_2$CN), 6.31 (d, *J* = 8.5 Hz, 2H, Br-C-(CHC*H*)$_2$C), 2.66 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 1.97 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.43, 167.83, 151.45, 150.29, 132.32, 129.34, 123.89, 120.92, 118.66, 117.13, 21.96, 15.58, 13.22. **ESI-HRMS (m/z):** calcd. for $C_{17}H_{17}BrN_2H^+$, 329.0653; found, 329.0652 (diff. 0.0001).

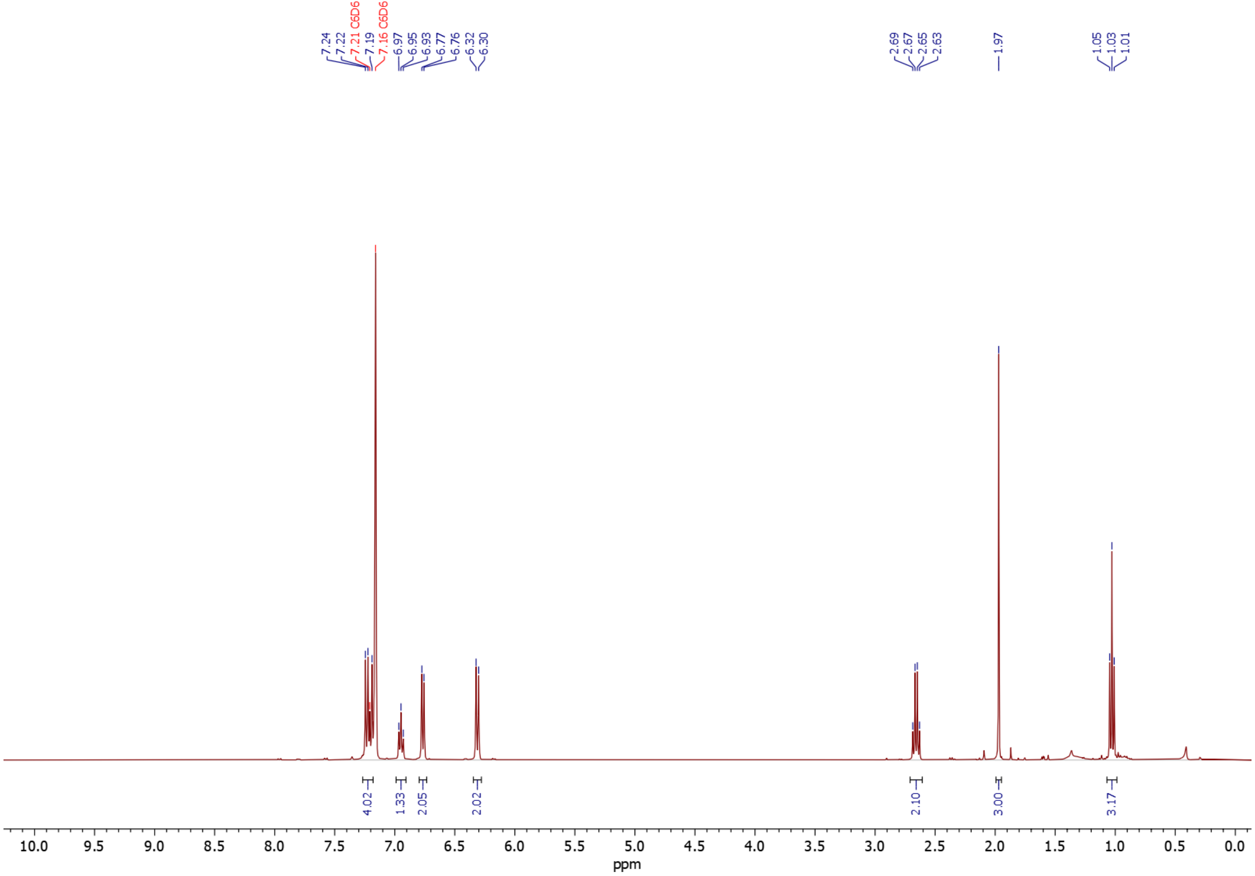


Figure S13. ^{1}H NMR spectrum of **3e** in C_6D_6.

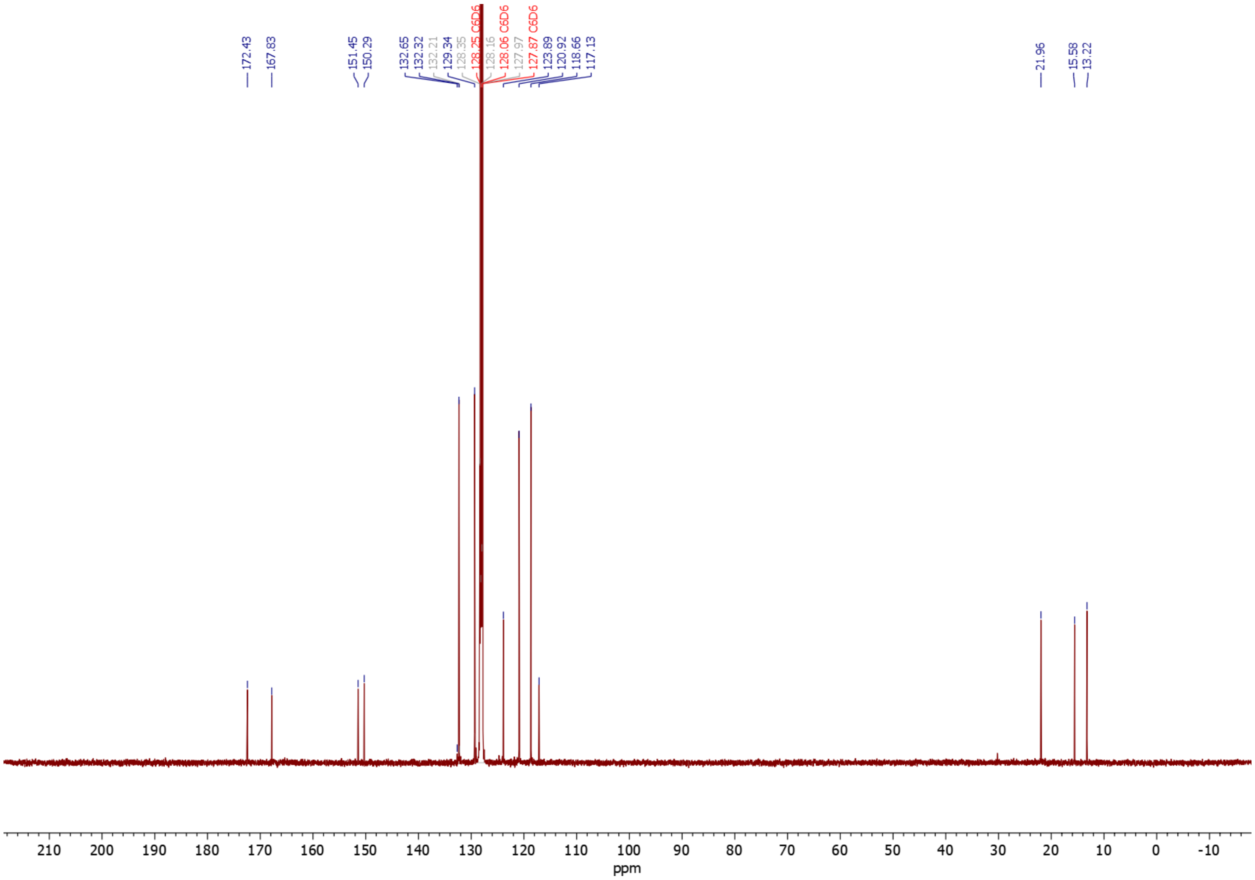
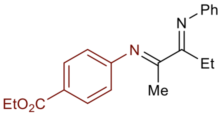


Figure S14. ^{13}C NMR spectrum of **3e** in C_6D_6.

(2E,3E)-*N*^{2}-(4-ethoxycarbonyphenyl)-*N*^{3}-phenylpentane-2,3-diimine (**3f)**



Red-orange oil, 45.9 mg. 71% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 8.18 (d, *J* = 8.5 Hz, 2H, $CH_3CH_2OC(O)$-C-$(CHCH)_2C$), 7.20 (t, *J* = 7.9 Hz, 2H, CH$(CHCH)_2$CN), 6.95 (t, *J* = 7.4 Hz, 1H, C*H*$(CHCH)_2$CN), 6.77 (d, *J* = 7.0 Hz, 2H, CH$(CHCH)_2$CN), 6.58 (d, *J* = 8.4 Hz, 2H, $CH_3CH_2OC(O)$-C-$(CHCH)_2C$), 4.18 (q, *J* = 7.1 Hz, 2H, $CH_3CH_2OC(O)$-C-$(CHCH)_2C$), 2.65 (q, *J* = 7.6 Hz, 2H, CH_2CH_3), 1.98 (s, 3H, CH_3), 1.07 (t, *J* = 7.1 Hz, 3H, $CH_3CH_2OC(O)$-C-$(CHCH)_2C$), 1.03 (t, *J* = 7.6 Hz, 3H, CH_2CH_3). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.24, 167.54, 166.06, 155.51, 151.39, 131.27, 129.34, 126.70, 123.93, 118.67, 118.62, 60.71, 21.97, 15.74, 14.40, 13.21. **ESI-HRMS (m/z):** calcd. for $C_{20}H_{22}N_2O_2H^+$, 345.1579; found, 345.1570 (diff. 0.0009).

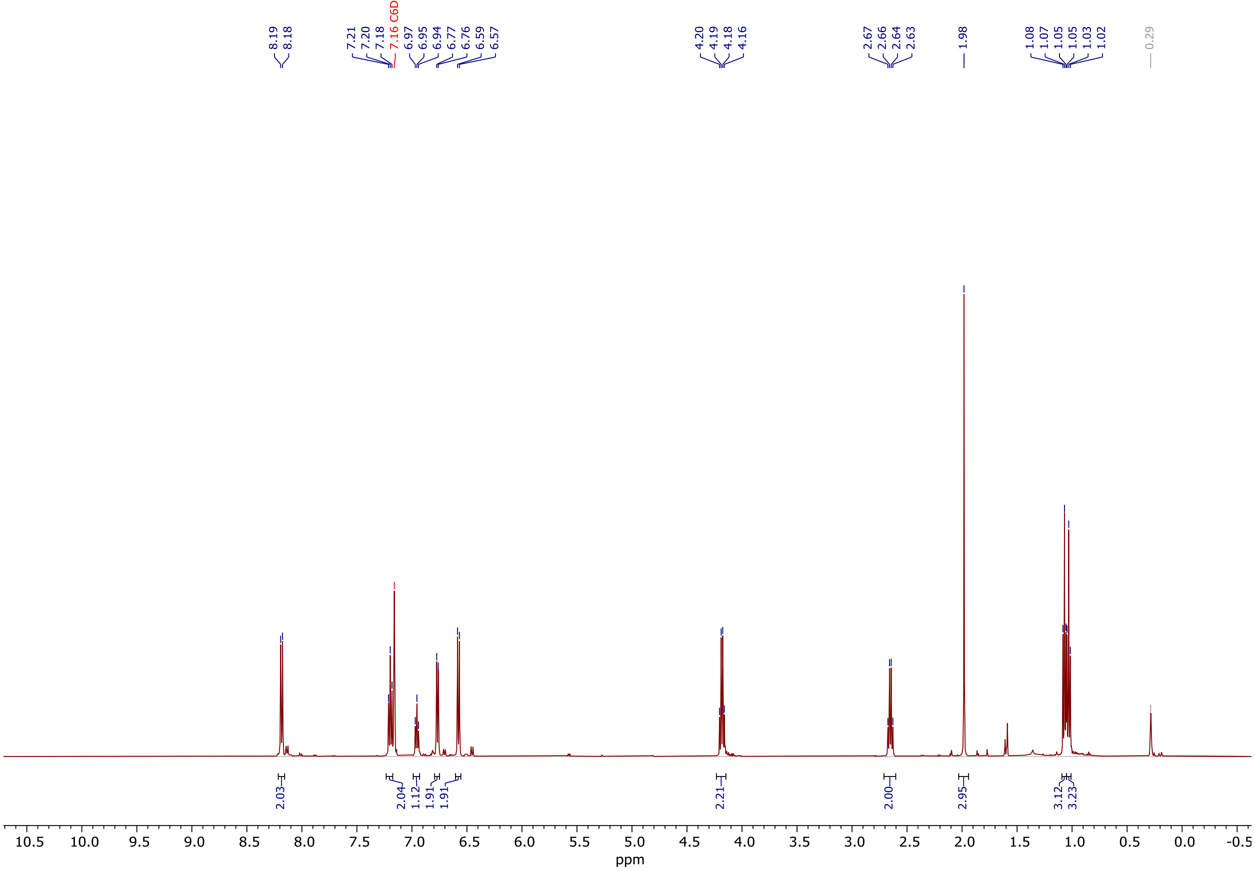


Figure S15. ^{1}H NMR spectrum of **3f** in C_6D_6.

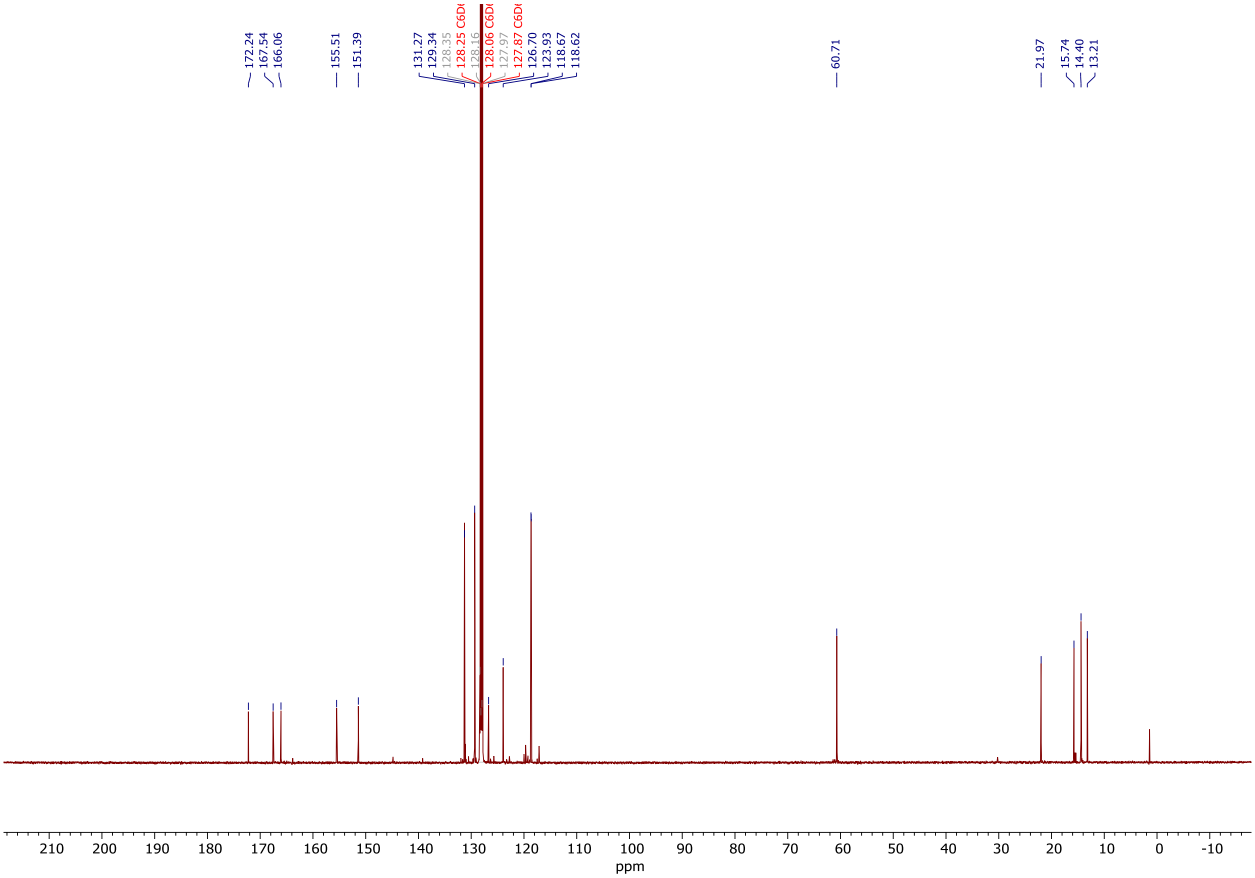
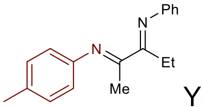


Figure S16. ^{13}C NMR spectrum of **3f** in C_6D_6.

(2E,3E)-N^3-phenyl-*N*^{2}-(*p*-tolyl)pentane-2,3-diimine (**3g)**



Yellow oil, 44.2 mg. 84% isolated yield. **^{1}H NMR (400 MHz, C_6D_6)** δ 7.22 – 7.16 (m, 2H, CH(C*H*CH)$_2$CN), 7.00 (d, *J* = 8.1 Hz, 2H, CH_3-C-(C*H*CH)$_2$C), 6.94 (tt, *J* = 7.4, 1.1 Hz, 1H, C*H*(CHCH)$_2$CN), 6.78 (dd, *J* = 8.4 Hz, 1.1 Hz, 2H, CH(CHC*H*)$_2$CN), 6.69 (d, *J* = 8.1 Hz, 2H, CH_3-C-(CHC*H*)$_2$C), 2.75 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.16 (s, 3H, C*H*$_3$), 2.14 (s, 3H, C*H*$_3$), 1.09 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.86, 167.10, 151.71, 149.06, 133.31, 129.86, 129.29, 123.68, 119.36, 118.75, 22.05, 20.88, 15.58, 13.32. **ESI-HRMS (m/z):** calcd. for $C_{18}H_{20}N_2H^+$, 265.1705; found, 265.1705.

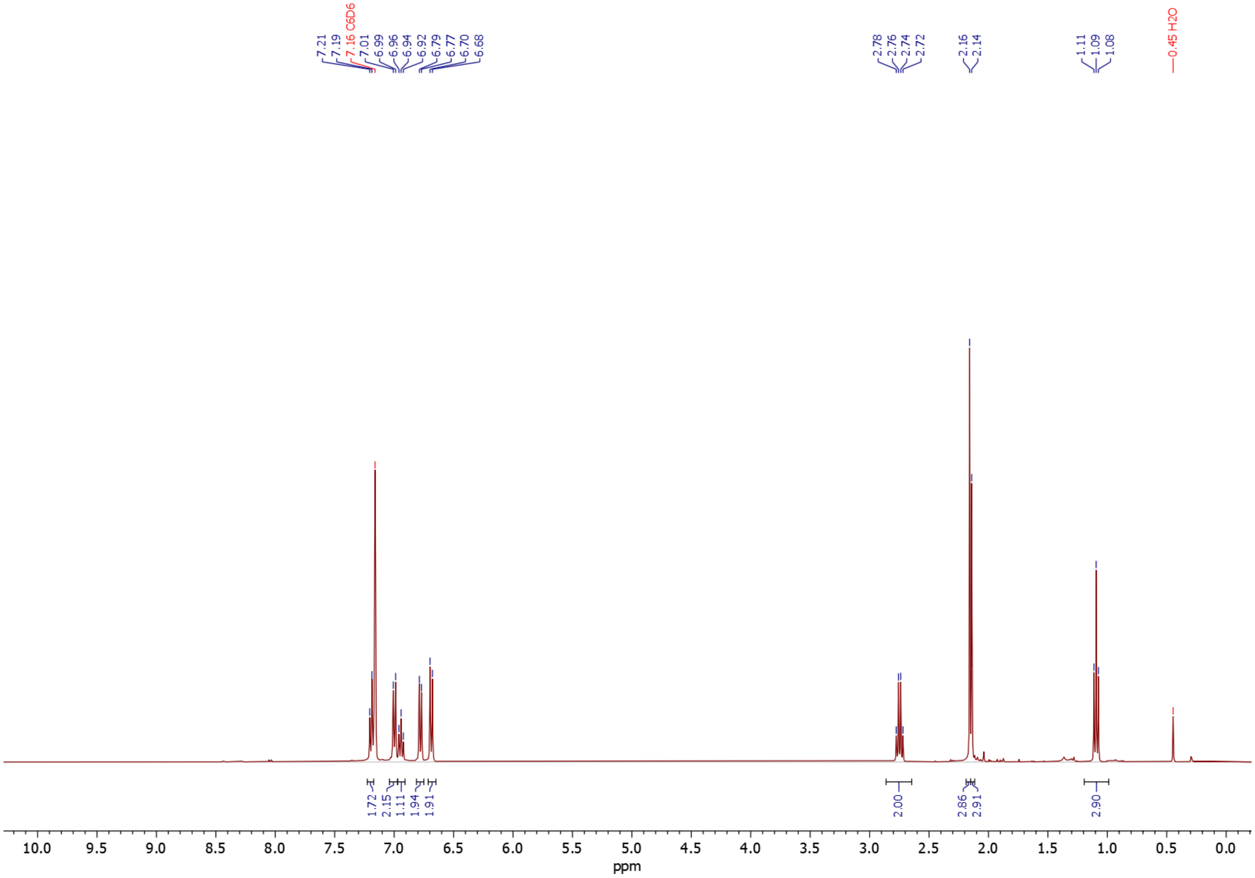


Figure S17. ^{1}H NMR spectrum of **3g** in C_6D_6.

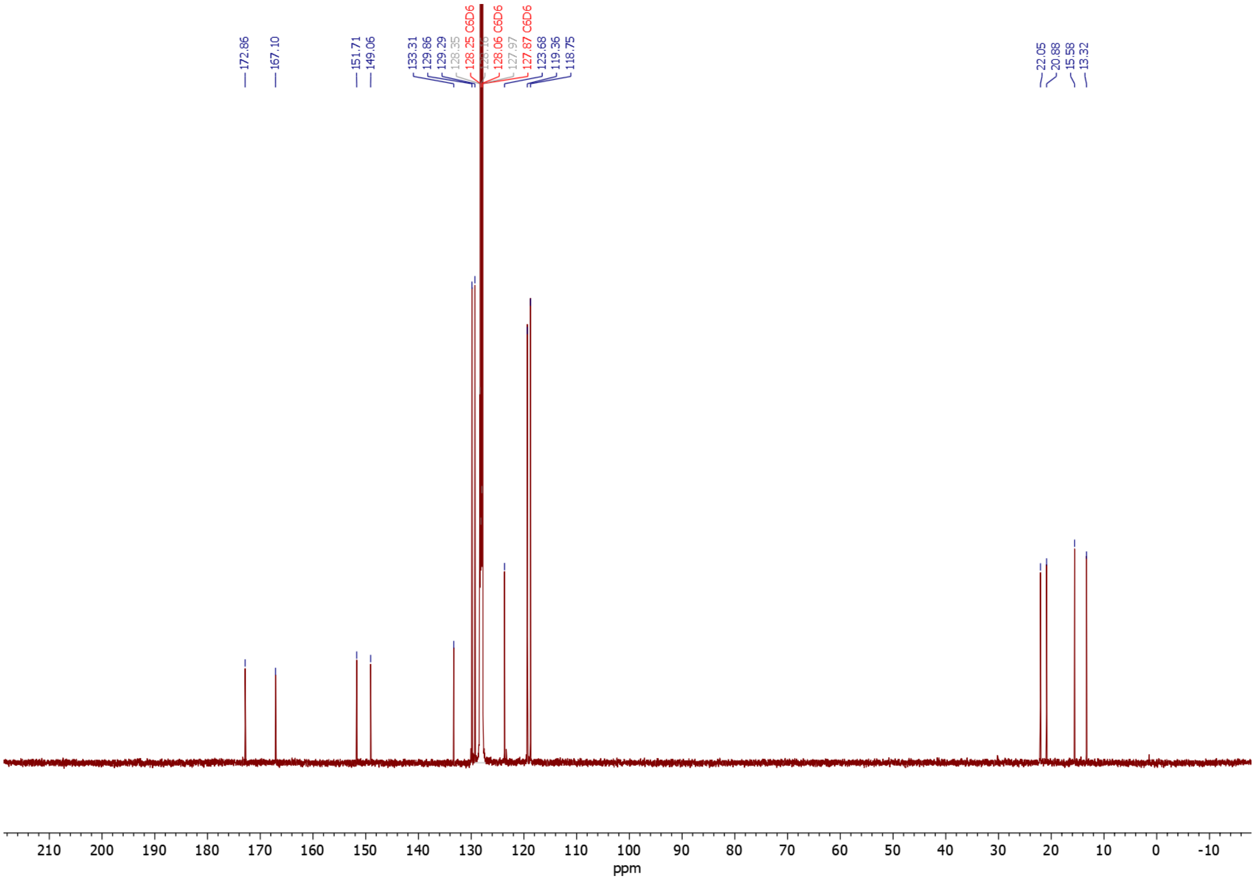
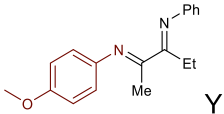


Figure S18. ^{13}C NMR spectrum of **3g** in C_6D_6.

(2E,3E)-*N*^{2}-(4-methoxyphenyl)-*N*^{3}-phenylpentane-2,3-diimine (**3h)**



Yellow solid, 46.2 mg. 82% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.19 (t, *J* = 7.6 Hz, 2H, CH(C*H*CH)$_2$CN), 6.95 (t, *J* = 7.5 Hz, 1H, C*H*(CHCH)$_2$CN), 6.79 (m, 4H, Ar-*H*), 6.72 (d, *J* = 8.4 Hz, 2H, CH$_3$O-C-(CHC*H*)$_2$C), 3.34 (s, 3H, C*H$_3$*O-C-(CHCH)$_2$C), 2.77 (q, *J* = 7.5 Hz, 2H, CH$_3$C*H$_2$*), 2.19 (s, 3H, C*H$_3$*), 1.11 (t, *J* = 7.5 Hz, 3H, C*H$_3$*CH$_2$). **^{13}C NMR (126 MHz, C_6D_6)** δ 173.00, 166.98, 157.14, 151.79, 144.47, 129.29, 123.65, 121.10, 118.77, 114.62, 55.01, 22.07, 15.60, 13.34. **ESI-HRMS (m/z):** calcd. for $C_{18}H_{20}N_2ONa^+$, 303.1473; found, 303.1467 (diff. 0.0006).

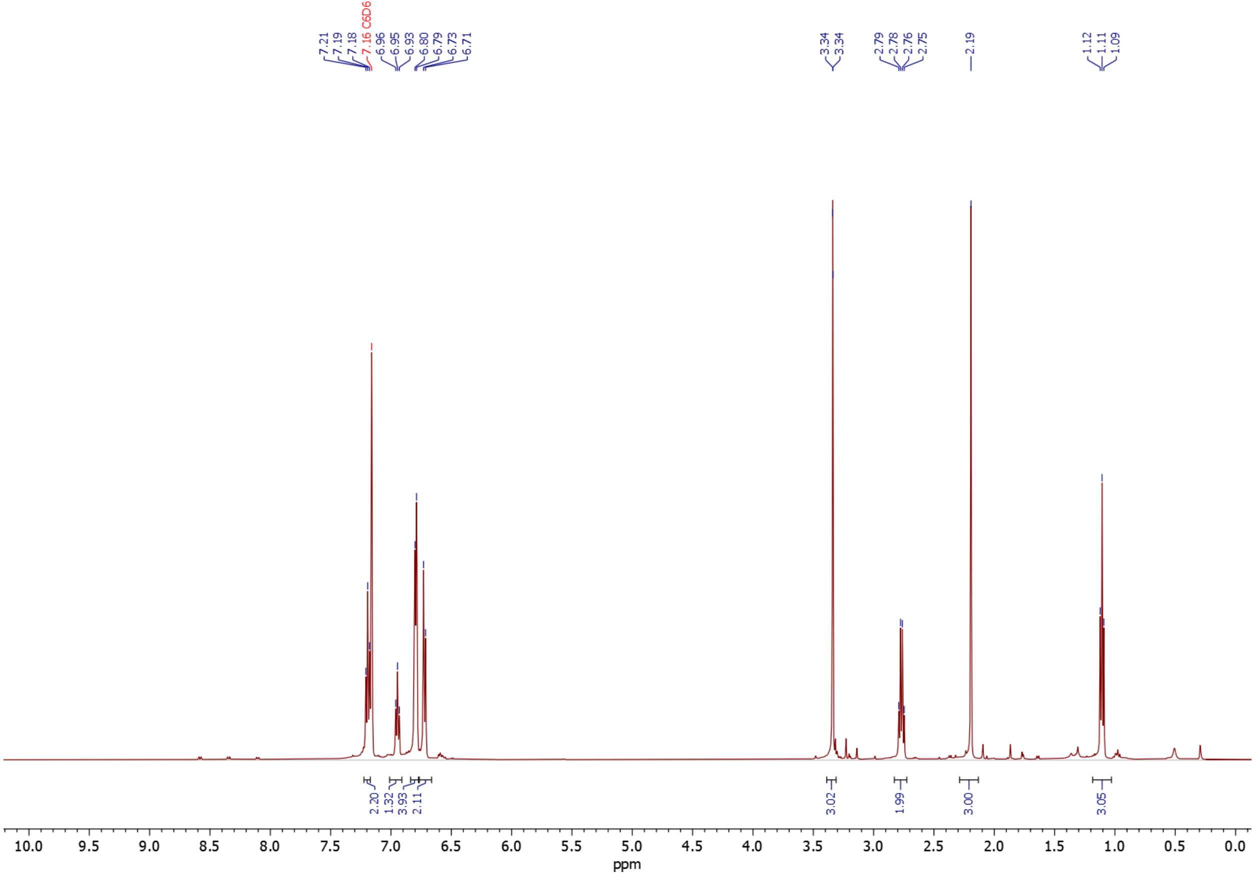


Figure S19. ^{1}H NMR spectrum of **3h** in C_6D_6.

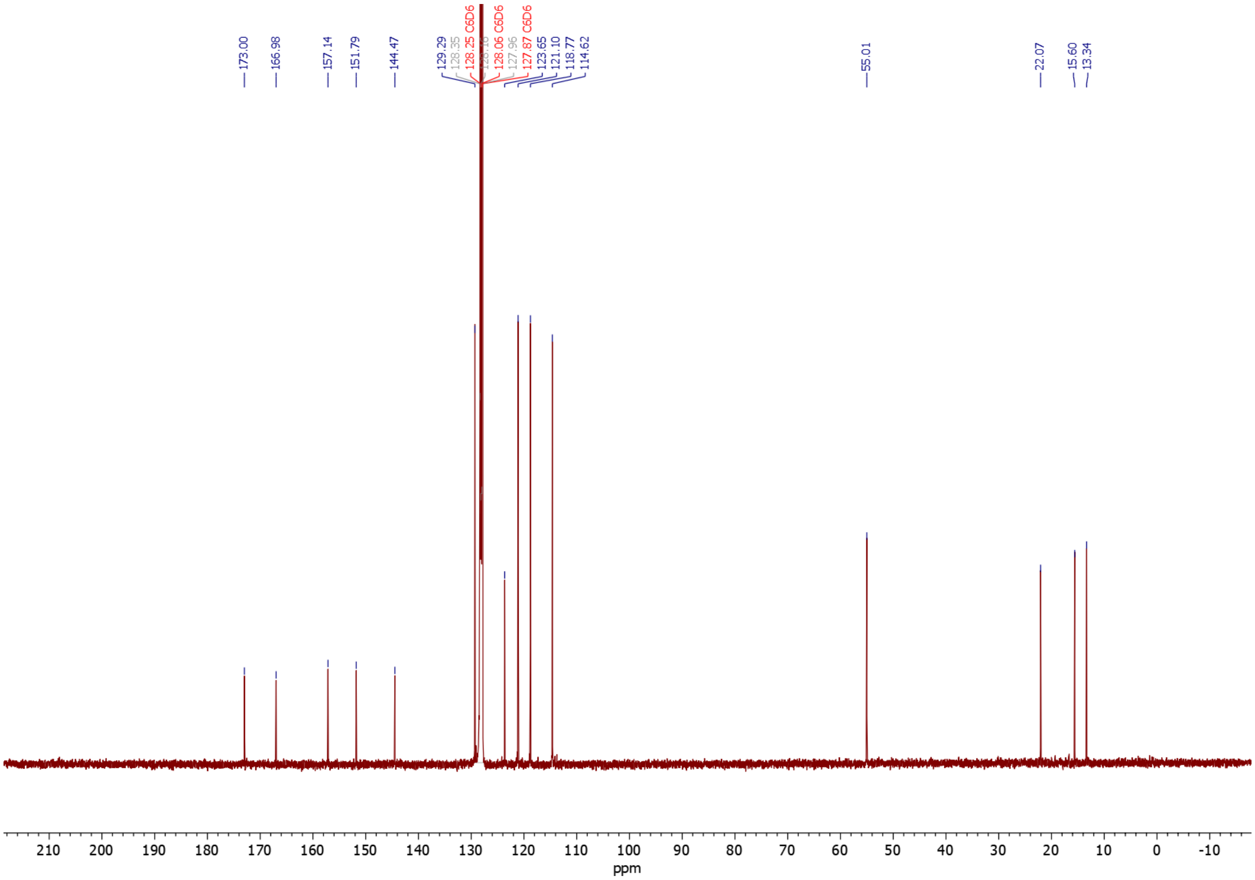
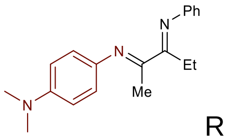


Figure S20. ^{13}C NMR spectrum of **3h** in C_6D_6.

(2E,3E)-N^2-(4-*N,N*-dimethyl)-N^3-phenylpentane-2,3-diimine (**3i**) **(Not isolated)**



Red oil. Not isolated, but NMR and GC-MS of reaction mixture after workup is provided. The unknown product is likely to be a derivative of the protonated ligand precursor of **1**, given its mass by GC-MS, which is the same mass but with a different fragmentation pattern.

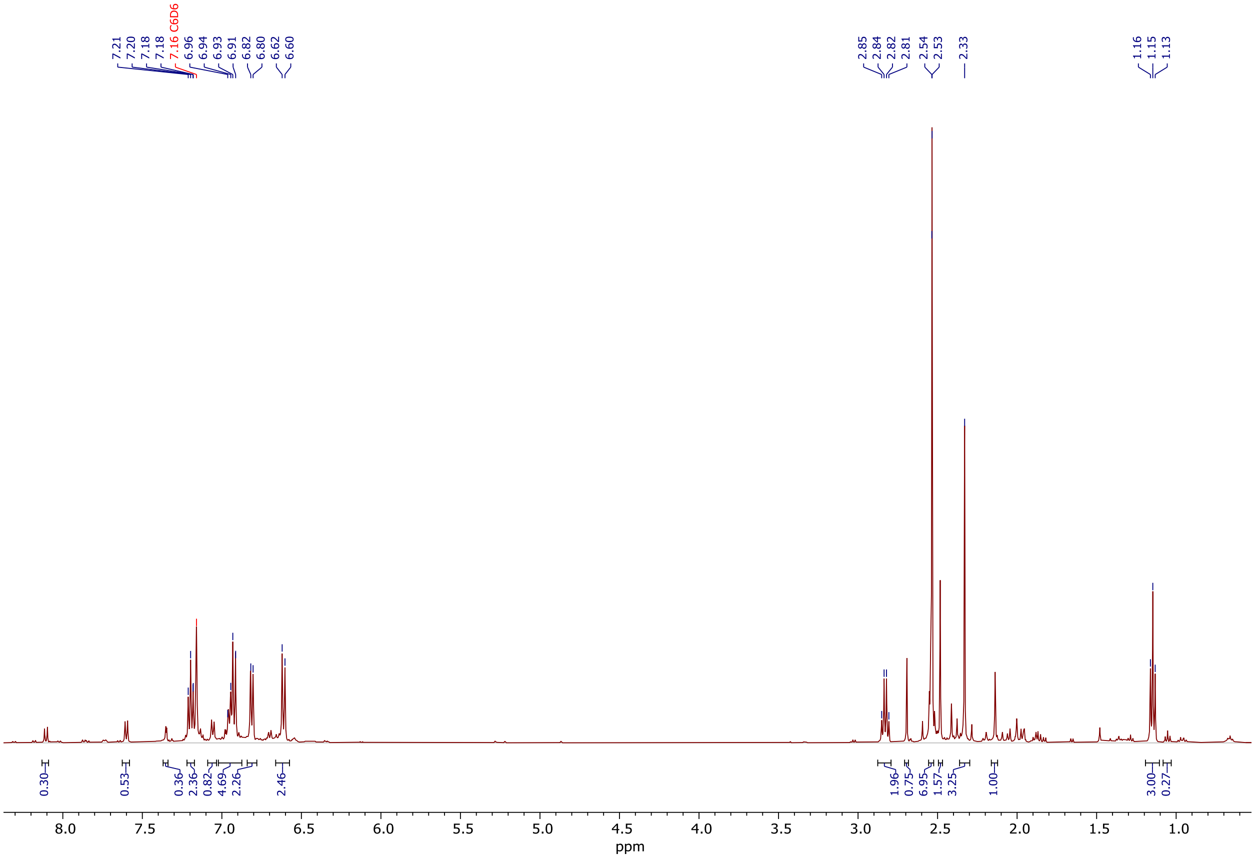


Figure S21. ^{1}H NMR spectrum of **3i** in C_6D_6.

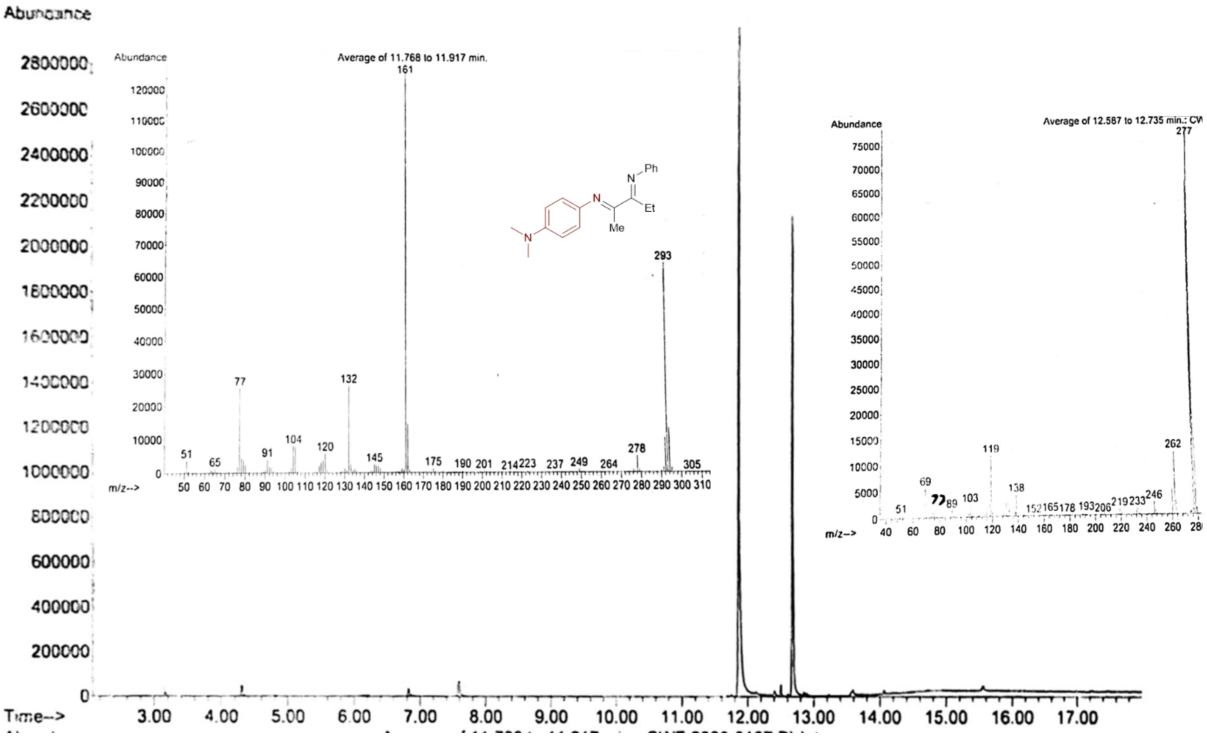
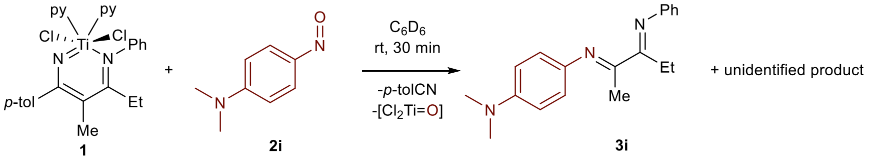


Figure S22. GC-MS of **3i** reaction mixture after workup.

(2E,3E)-*N*^{2}-(4-*N,N*-dimethyl)-*N*^{3}-phenylpentane-2,3-diimine (**3i**) **(NMR scale)**



In-situ Procedure: Diazatitanacyclohexadiene **1** (12.5 mg, 0.023 mmol) and internal standard 1,3,5-trimethoxybenzene (TMB) (4.5 mg, 0.027 mmol) were added to an NMR tube and dissolved in 0.5 mL C_6D_6, then **2i** 4.4 mg, 0.029 mmol, 1.3 equiv.) was added. A ^{1}H NMR spectrum was recorded after 30 min. Diimine **3i** was observed to have formed in an 49% yield, as well as some unidentified products.

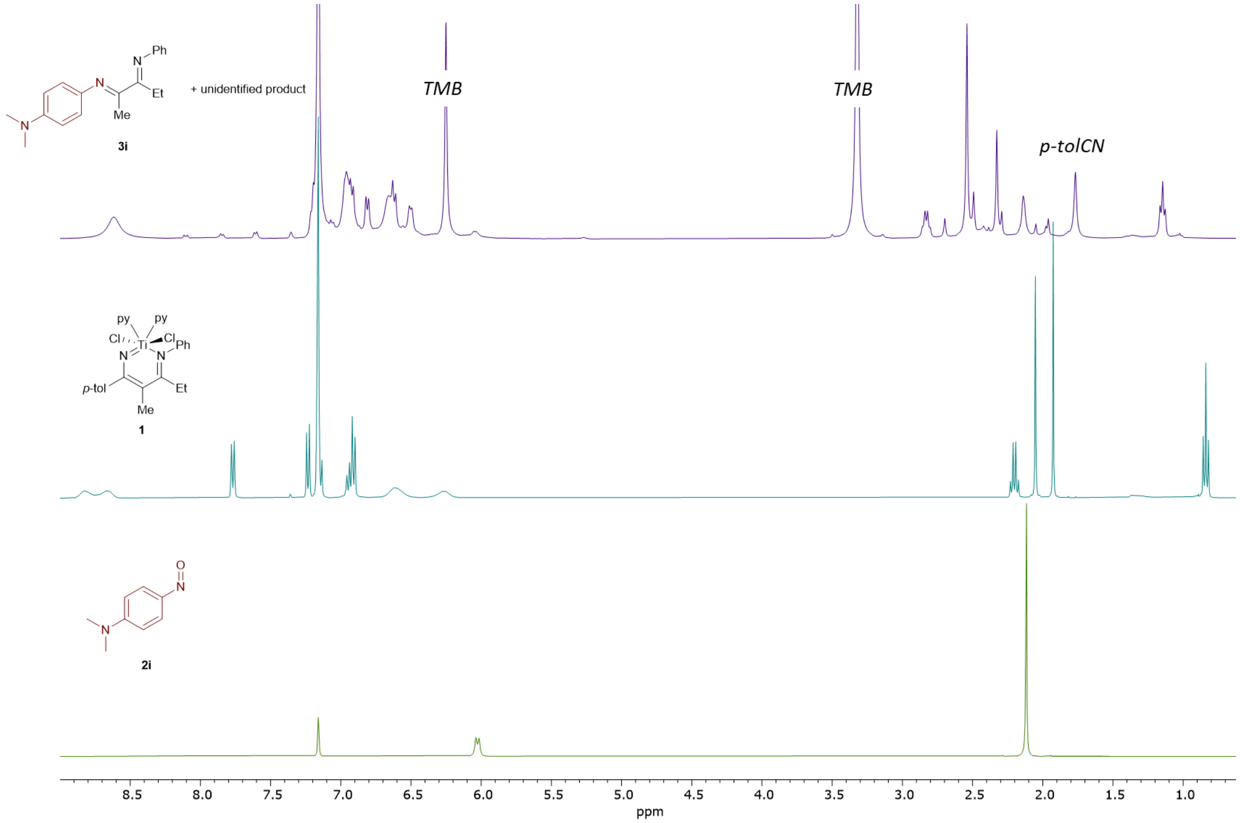


Figure S23. Stacked ^{1}H NMR spectra (C_6D_6) of additon of **2i** to **1**; Bottom (green trace): **2i** prior to addition; Middle (blue trace): **1** prior to addition; Top (purple trace): After addition of **2i** to **1**, t = 0.5 h at room temperature, showing 49% yield of **3i** according to 1,3,5-trimethoxybenzene standard, with unidentified product also formed.

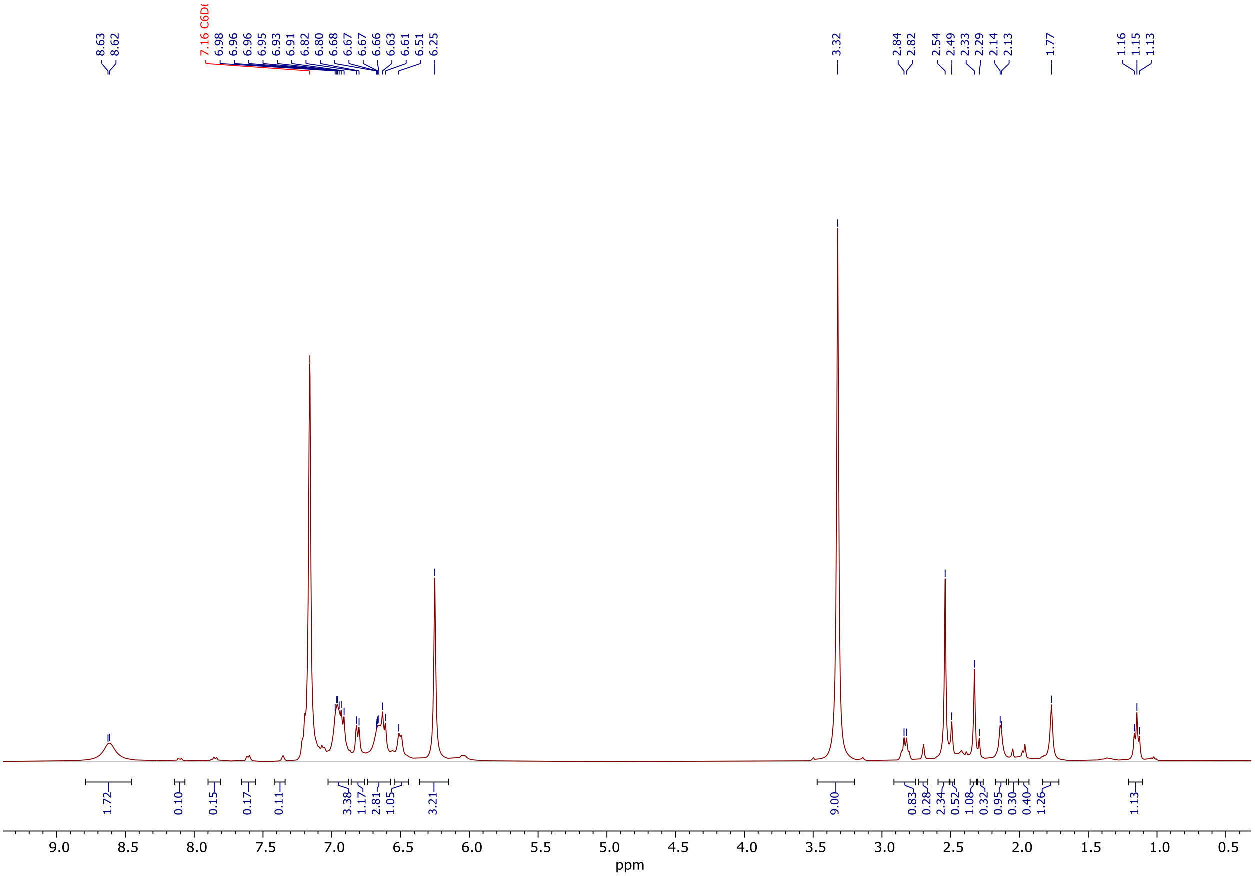
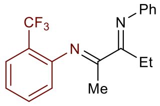


Figure S24. ^{1}H NMR spectrum (C_6D_6) of additon of **2i** to **1**, showing 49% yield of **3i** according to 1,3,5-trimethoxybenzene standard, with unidentified product also formed.

(2E,3E)-*N*^{3}-phenyl-*N*^{2}-(*o*-(trifluoromethyl)phenyl)pentane-2,3-diimine (**3j**)



Orange-yellow oil, 53.8 mg. 78% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.46 (d, *J* = 7.9 Hz, 1H, NCCHCHCHC*H*CCF$_3$), 7.20 – 7.12 (m, 2H, CH(C*H*CH)$_2$CN), 6.99 (t, *J* = 7.4 Hz, 1H, NCCHC*H*CHCHCCF$_3$), 6.93 (tt, *J* = 7.4, 1.2 Hz, 1H, C*H*(CHCH)$_2$CN), 6.72 (d, *J* = 7.2 Hz, 2H, CH(CHC*H*)$_2$CN), 6.72 – 6.67 (m, 1H, NCCHCHC*H*CHCCF$_3$), 6.32 (d, *J* = 7.9 Hz, 1H, NCC*H*CHCHCHCCF$_3$), 2.72 (q, *J* = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 2.05 (s, 3H, C*H*$_3$), 1.12 (t, *J* = 7.6 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.27, 169.19, 151.27, 149.82 (q, *J* = 1.7 Hz), 132.72, 129.28, 126.66 (q, *J* = 5.1 Hz), 124.76 (q, *J* = 272.5 Hz),123.92, 123.49, 119.38 (q, *J* = 30.5 Hz), 119.25, 118.68, 21.93, 16.35, 12.77. **^{19}F NMR (471 MHz, C_6D_6)** δ -61.69 (vs. TFA δ -77.80). **ESI-HRMS (m/z):** calcd. for $C_{18}H_{17}F_3N_2H^+$, 319.1422; found, 319.1440 (diff. 0.0018).

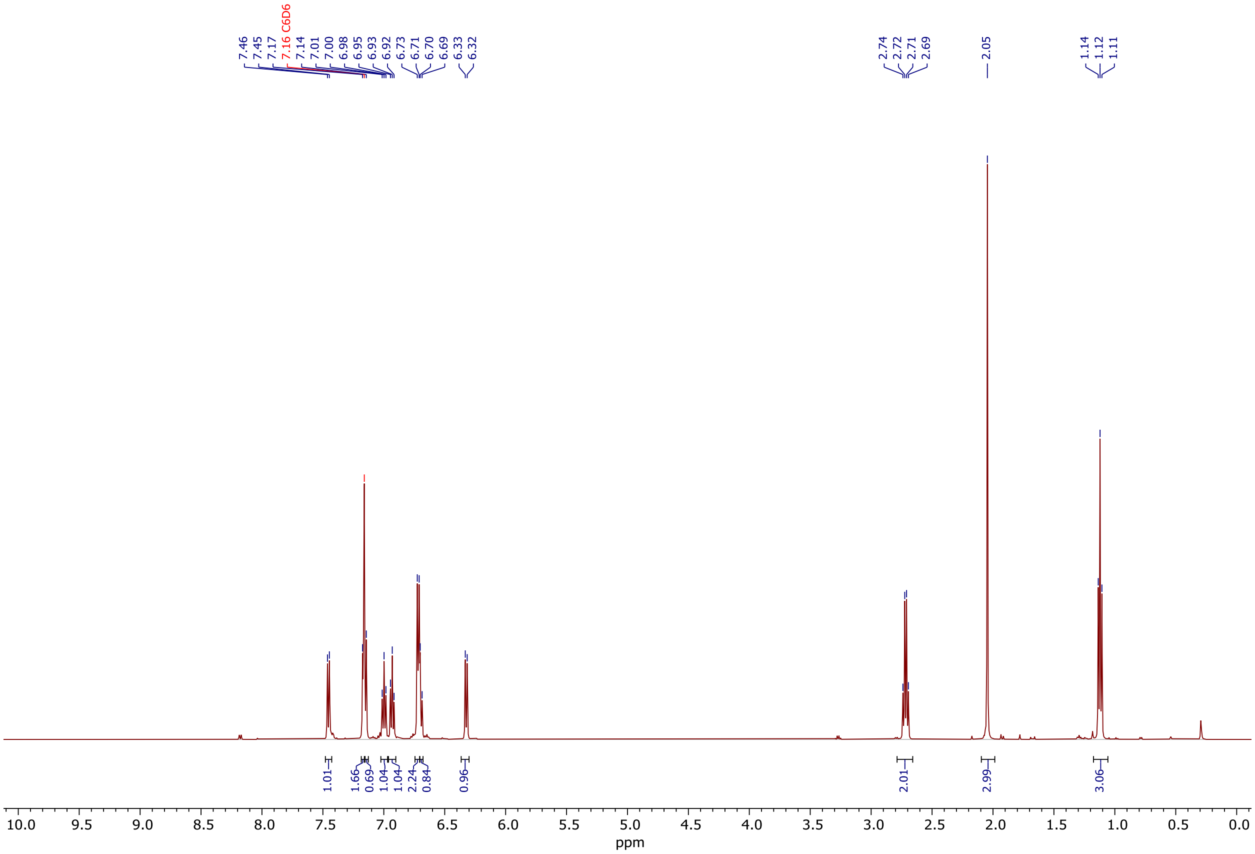


Figure S25. ^{1}H NMR spectrum of **3j** in C_6D_6.

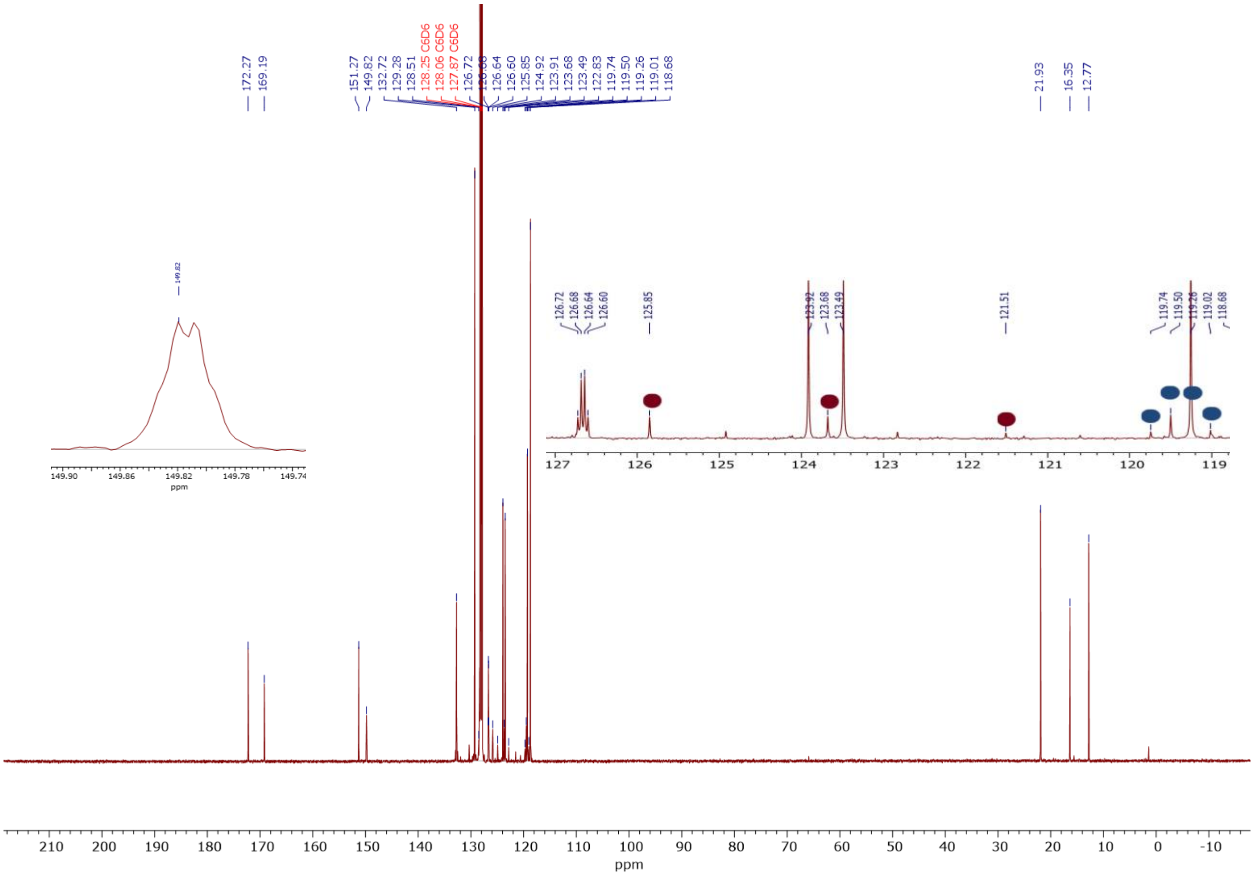


Figure S26. ^{13}C NMR spectrum of **3j** in C_6D_6, inset shows quartets from ^{13}C-^{19}F coupling.

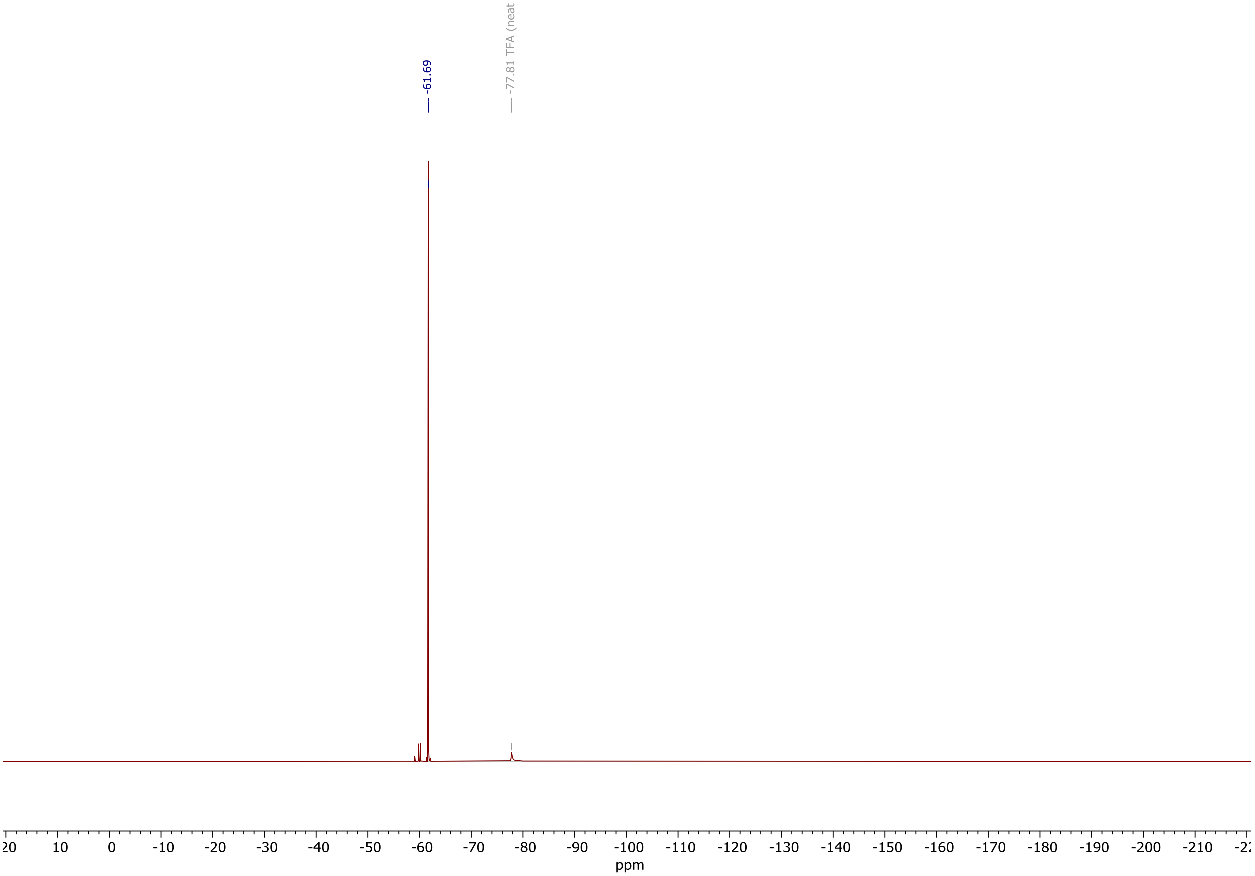
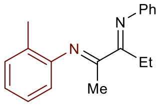


Figure S27. ^{19}F NMR spectrum of **3j** in C_6D_6 with trifluoroacetic acid (neat) reference capillary (δ -77.80).

(2E,3E)-N^3-phenyl-*N*^{2}-(*o*-tolyl)pentane-2,3-diimine (**3k**)



Red-orange oil, 39.0 mg. 74% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.21 – 7.16 (m, 2H, CH(C*H*CH)$_2$CN), 7.13 – 7.02 (m, 2H, Ar-*H*), 6.99 – 6.90 (m, 2H, Ar-*H*), 6.77 (dd, *J* = 8.6, 1.2 Hz, 2H, CH(CHC*H*)$_2$CN), 6.55 (dd, *J* = 7.7, 1.3 Hz, 1H, NCC*H*CHCHCHCCH$_3$), 2.75 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.06 (s, 3H, C*H*$_3$), 2.05 (s, 3H, C*H*$_3$), 1.09 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.56, 166.95, 151.60, 150.29, 130.80, 129.28, 126.84, 126.79, 124.17, 123.75, 118.77, 117.93, 22.00, 18.05, 15.81, 13.29. **ESI-HRMS (m/z):** calcd. for $C_{18}H_{20}N_2H^+$, 265.1705; found, 287.1687 (diff. 0.018).

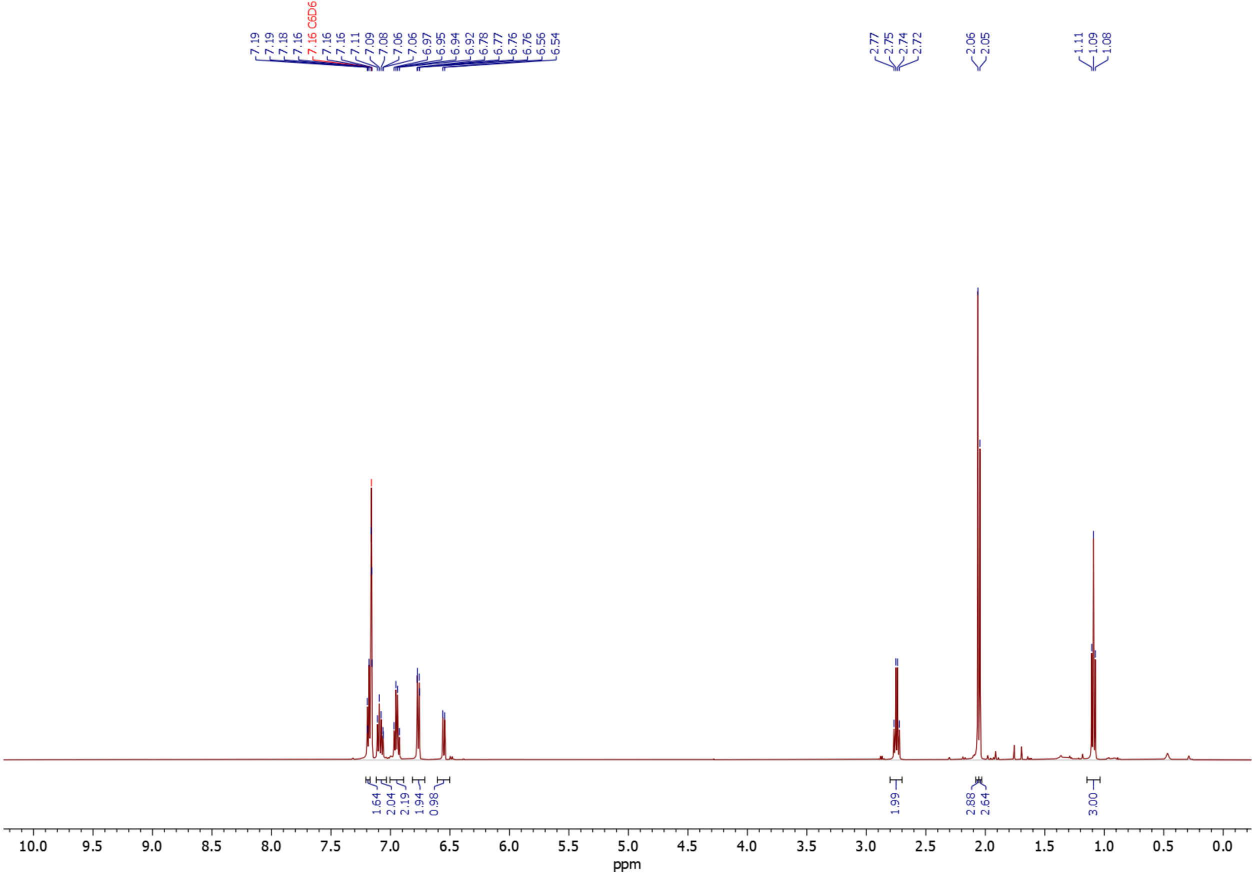


Figure S28. ^{1}H NMR spectrum of **3k** in C_6D_6.

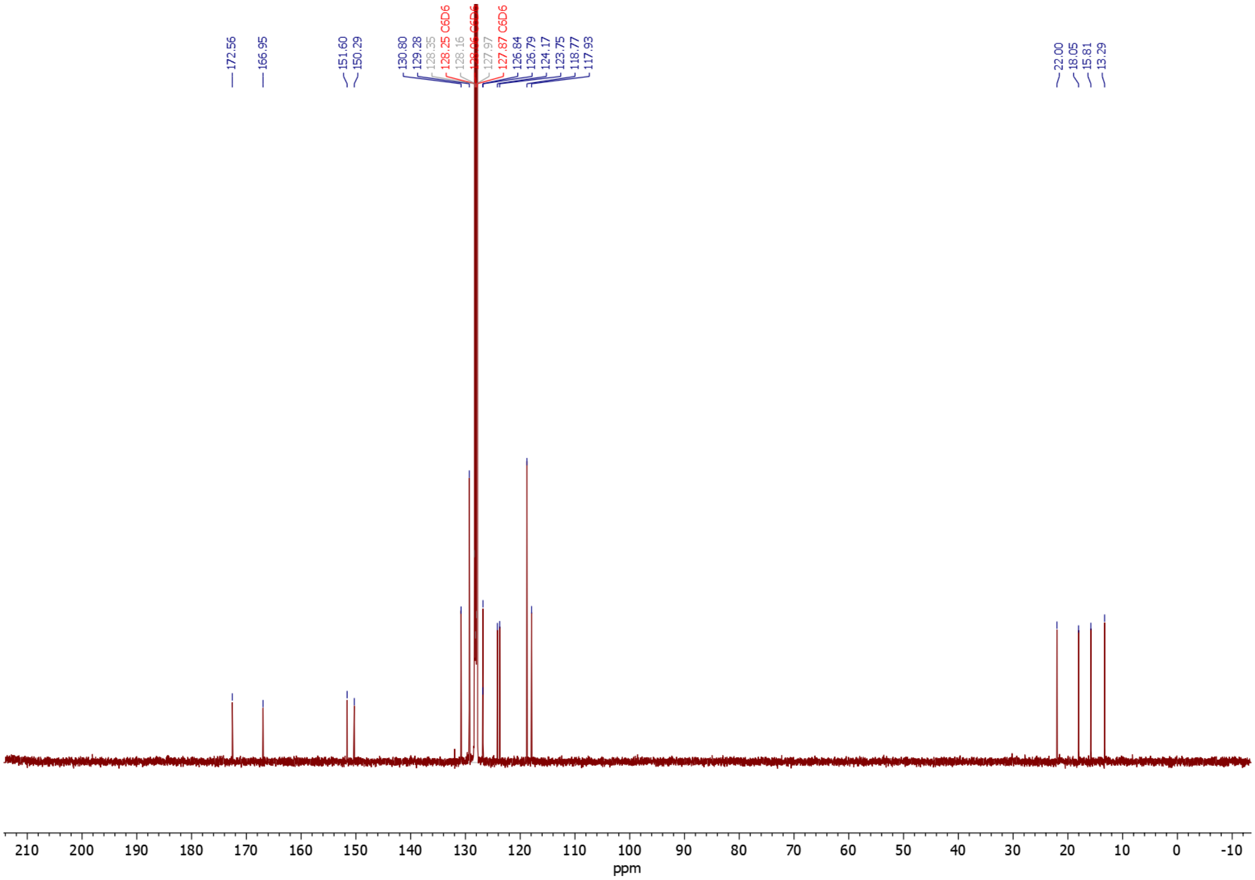
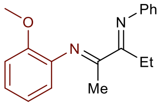
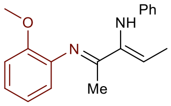


Figure S29. ^{13}C NMR spectrum of **3k** in C_6D_6.

(2E,3E)-*N*^{3}-phenyl-*N*^{2}-(*o*-methoxyphenyl)pentane-2,3-diimine (**3l**)





Orange oil, 41.5 mg. 74% isolated yield. Isolated as mixture of imine/enamine tautomers in a 6:1 ratio.

Diimine: **^{1}H NMR (500 MHz, C_6D_6)** δ 7.19 – 7.16 (m, 2H, CH(C*H*CH)$_2$CN), 7.16 – 7.14 (m, 1H, NCCHCHC*H*CHCOCH$_3$), 6.99 – 6.87 (m, 4H, Ar-*H*), 6.80 – 6.75 (m, 1H, NCCHCHCHC*H*COCH$_3$), 6.75 – 6.71 (m, 2H, CH(CHC*H*)$_2$CN), 6.66 – 6.60 (m, 1H, NCCHCHCHC*H*COCH$_3$), 3.28 (s, 3H, OC*H*$_3$), 2.80 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.18 (s, 3H, C*H*$_3$), 1.17 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 172.73, 168.48, 151.74, 148.63, 140.84, 129.22, 124.79, 123.61, 121.23, 120.06, 118.79, 111.96, 55.16, 22.21, 16.17, 13.27. **ESI-HRMS (m/z):** calcd. for $C_{18}H_{20}N_2H^+$, 281.1654; found, 281.1652 (diff. 0.0002).

Enamine: **^{1}H NMR (500 MHz, C_6D_6, aryl region buried, only <6 ppm assigned)** δ 5.61 (q, *J* = 7.2, 1H, C=C*H*CH$_3$), 3.23 (s, 3H, OC*H*$_3$), 1.80 (s, 3H, C*H*$_3$), 1.60 (d, *J* = 7.2 Hz, 3H, C=CHC*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 164.83, 149.31, 145.08, 140.62, 139.53, 129.13, 124.47, 121.33, 121.28, 119.67, 117.67, 117.28, 112.06, 55.20, 15.74, 15.56.

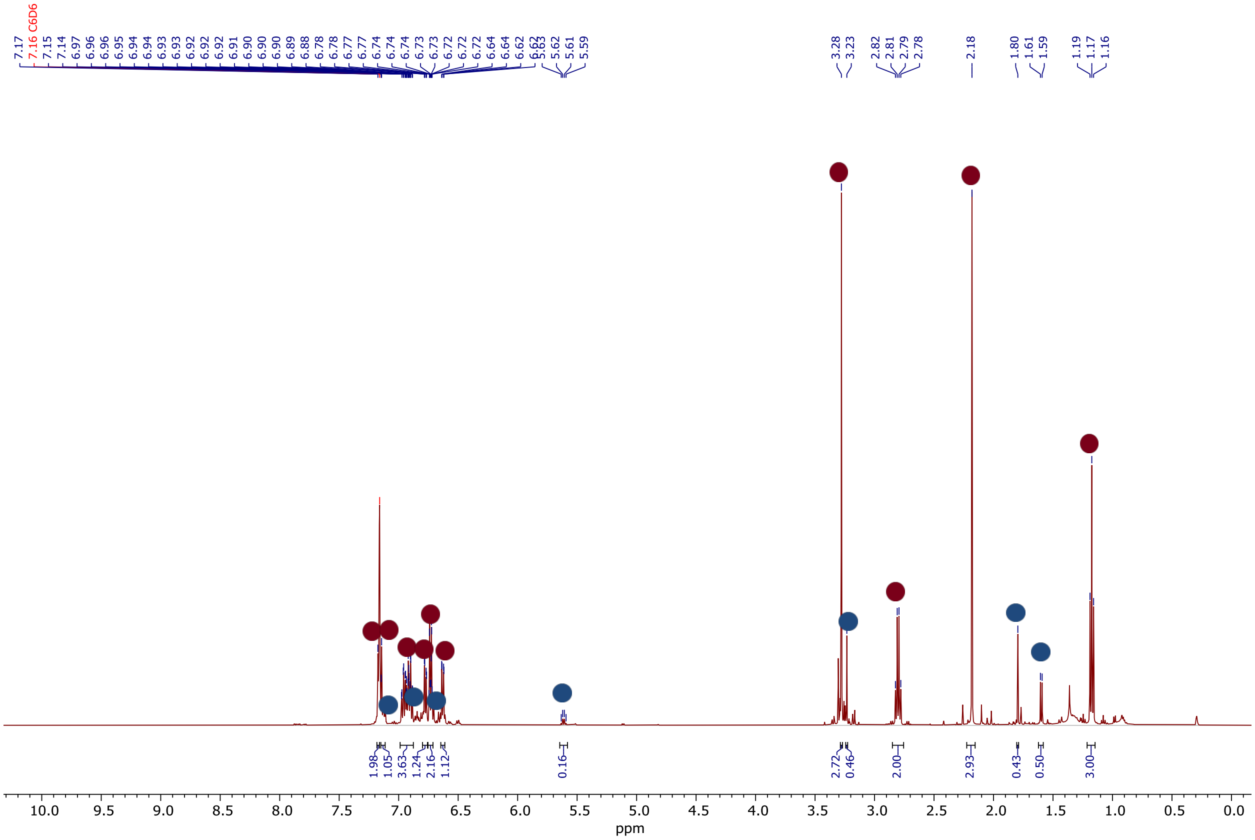


Figure S30. ^{1}H NMR spectrum of **3l** in C_6D_6 (Diimine denoted in red, enamine in blue).

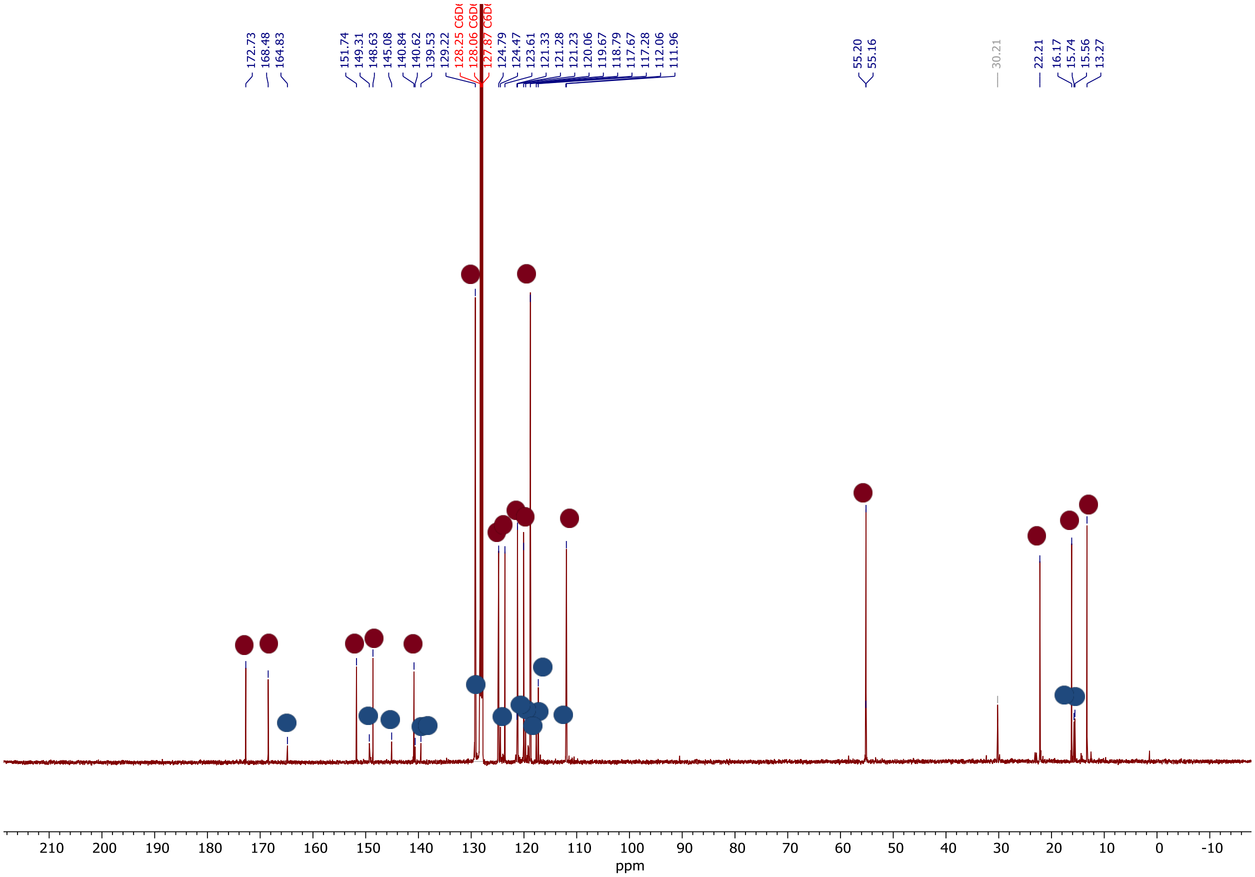
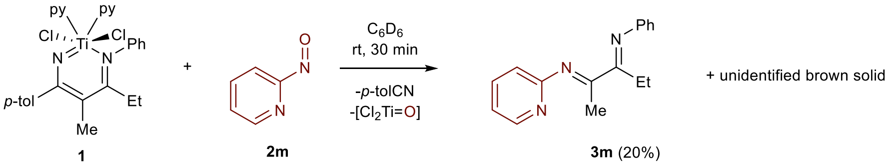


Figure S31. ^{13}C NMR spectrum of **3l** in C_6D_6.

(2E,3E)-*N^3*-phenyl-*N^2*-(pyridin-2-yl)pentane-2,3-diimine (**3m**) **(NMR scale)**



In-situ Procedure: Diazatitanacyclohexadiene **1** (12.8 mg, 0.023 mmol) and internal standard 1,3,5-trimethoxybenzene (TMB) (3.9 mg, 0.023 mmol) were added to an NMR tube and dissolved in 0.5 mL C_6D_6, then **2m** 3.2 mg, 0.03 mmol, 1.3 equiv.) was added. A ^{1}H NMR spectrum was recorded after 30 min. Diimine **3m** was observed to have formed in an 20% yield, which is small compared to the observed amount of *p*-tolunitrile (85%) (1:1 in all other examples). Free pyridine is also evident in the free spectrum (unlike in reactions of **1** with **2a** and other nitrosos). A large amount of insoluble brown solid was also observed to crash out of solution. It is possible the N of the heteronitroso fragment inhibits reactivity following p-tolunitrile elimination, perhaps through chelation, displacing the bound pyridine.

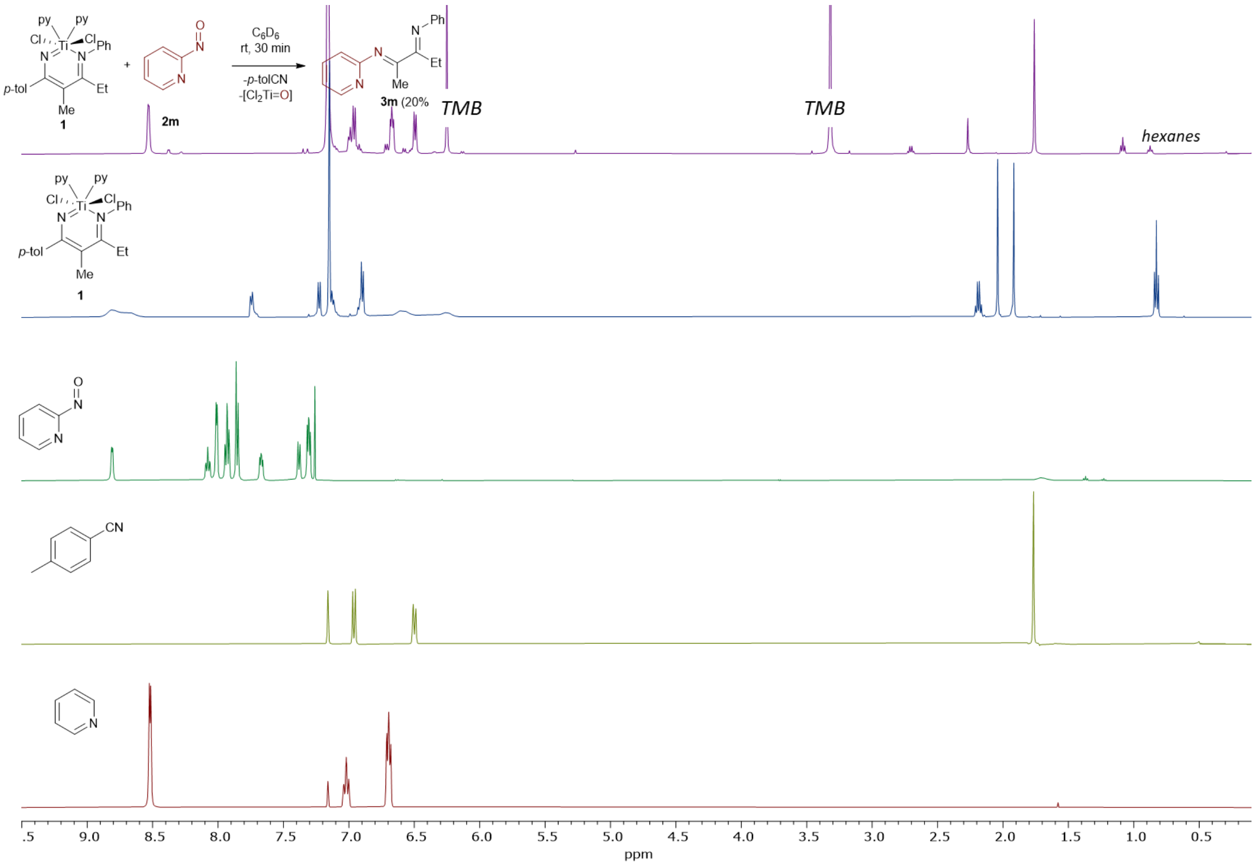


Figure S32. Stacked ^{1}H NMR spectra (C_6D_6) of additon of **2m** to **1**; Bottom (red trace): pyridine, Middle-bottom (light green trace): *p*-tolunitrile; Middle (green trace): **2m** prior to addition, Middle-top (blue trace): **1** prior to addition; Top (purple trace): reaction mixture showing **3m** in 20% yield, *p*-tolunitrile (85%), and free pyridine versus 1,3,5-trimethoxybenzene standard.

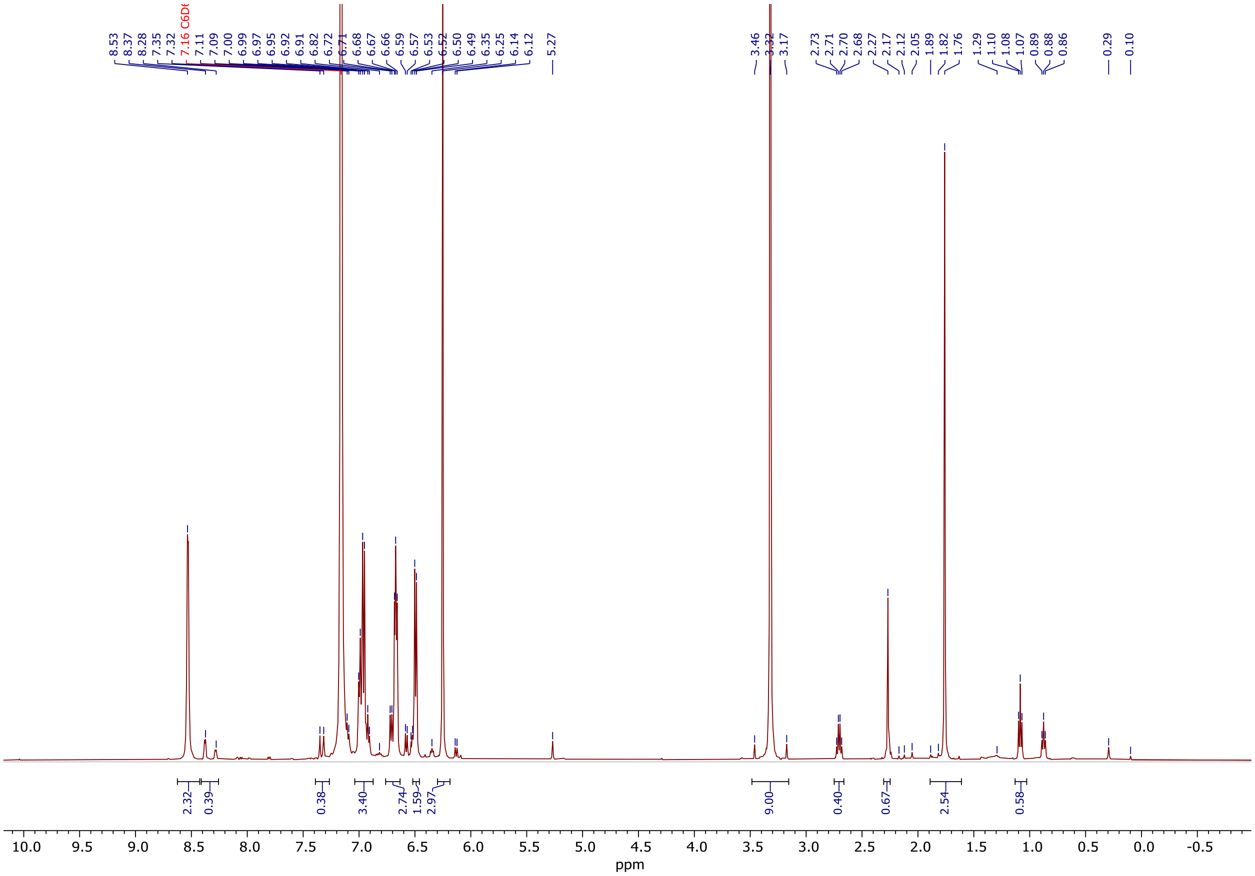
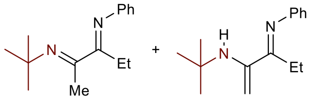


Figure S33. ^{1}H NMR spectrum (C_6D_6) of additon of **2m** to **1**, showing **3m** in 20% yield, *p*-tolunitrile (85%), and free pyridine versus 1,3,5-trimethoxybenzene standard.

(2E,3E)-*N*^{2}-(tert-butyl)-*N*^{3}-phenylpentane-2,3-diimine (**3n**)



Pale yellow oil, 31.6 mg. 71% isolated yield of mixture of imine/enamine tautomers in 4.1:1 ratio.

Diimine: **^{1}H NMR (500 MHz, C_6D_6)** δ 7.20 – 7.16 (m, 2H, $CH(C\mathit{H}CH)_2CN$), 6.91 (t, *J* = 7.4 Hz, 1H, $C\mathit{H}(CHCH)_2CN$), 6.76 (d, *J* = 7.7 Hz, 2H, $CH(CHC\mathit{H})_2CN$), 2.68 (q, *J* = 7.5 Hz, 2H, $C\mathit{H_2}CH_3$), 2.20 (s, 3H, $C\mathit{H_3}$), 1.27 (s, 9H, $(C\mathit{H_3})_3CN$), 1.01 (t, *J* = 7.5 Hz, 3H, $CH_2C\mathit{H_3}$)). **^{13}C NMR (126 MHz, C_6D_6)** δ 174.12, 162.89, 152.24, 129.24, 123.25, 118.87, 55.81, 30.27, 22.13, 16.63, 13.41. **ESI-HRMS (m/z):** calcd. for $C_{15}H_{22}N_2Na^+$, 253.1681; found, 253.1698 (diff. 0.0017).

Enamine: **^{1}H NMR (500 MHz, C_6D_6)** δ 7.10 (t, *J* = 7.3 Hz, 2H, $CH(C\mathit{H}CH)_2CN$), 6.87 (t, *J* = 7.4 Hz, 1H, $C\mathit{H}(CHCH)_2CN$), 6.67 (d, *J* = 7.7 Hz, 2H, $CH(CHC\mathit{H})_2CN$), 4.58 (s, 1H, $C{=}C\mathit{H_2}$), 4.55 (s, 1H, $C{=}C\mathit{H_2}$), 2.32 (q, *J* = 7.7 Hz, 2H, $C\mathit{H_2}CH_3$), 1.28 (s, 9H, $CC\mathit{H_3}$), 0.95 (t, *J* = 7.6 Hz, 3H, $CH_2C\mathit{H_3}$). **^{13}C NMR (126 MHz, C_6D_6)** δ 168.89, 151.71, 143.56, 129.25, 123.29, 119.40, 87.05, 49.83, 28.84, 22.01, 14.53.

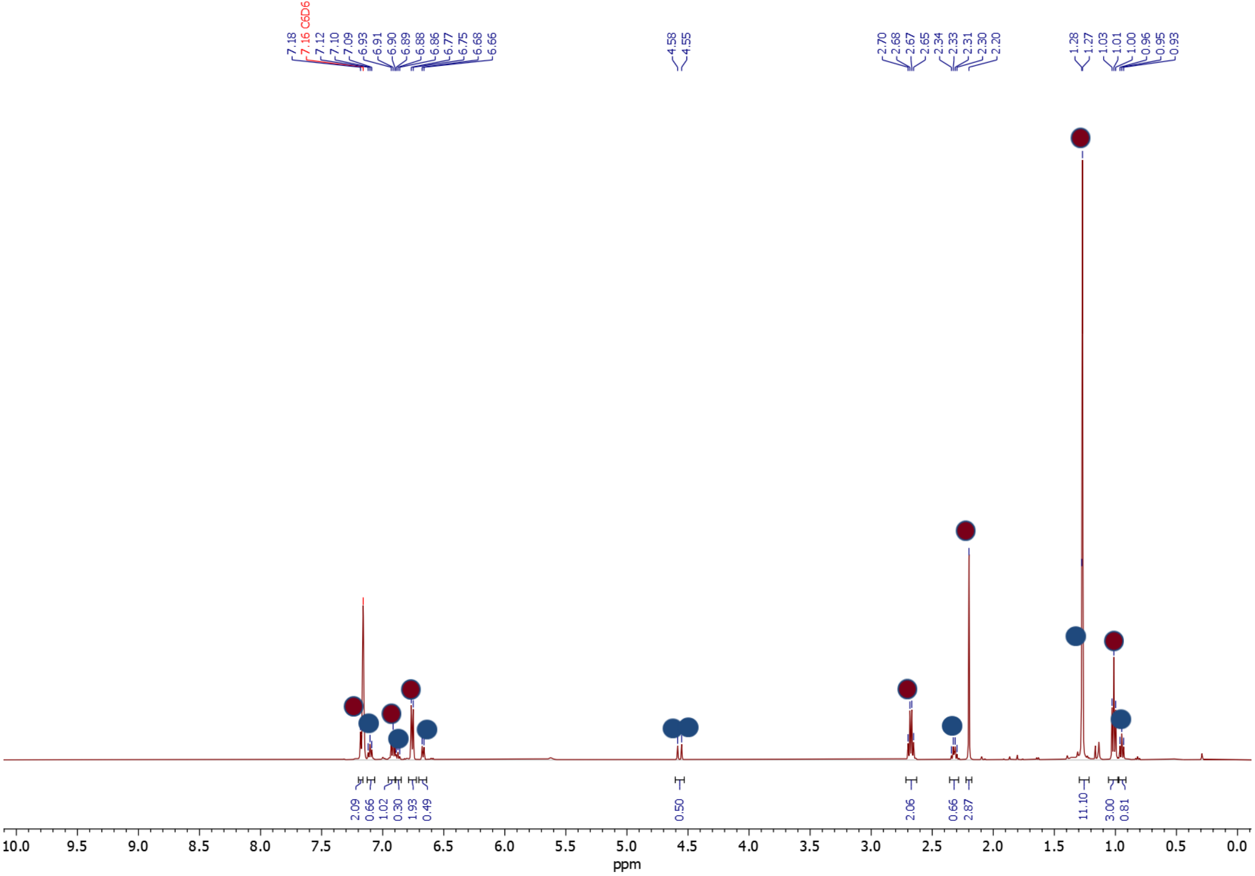


Figure S34. ^{1}H NMR spectrum of **3n** in C_6D_6 (Diimine denoted in red, enamine in blue).

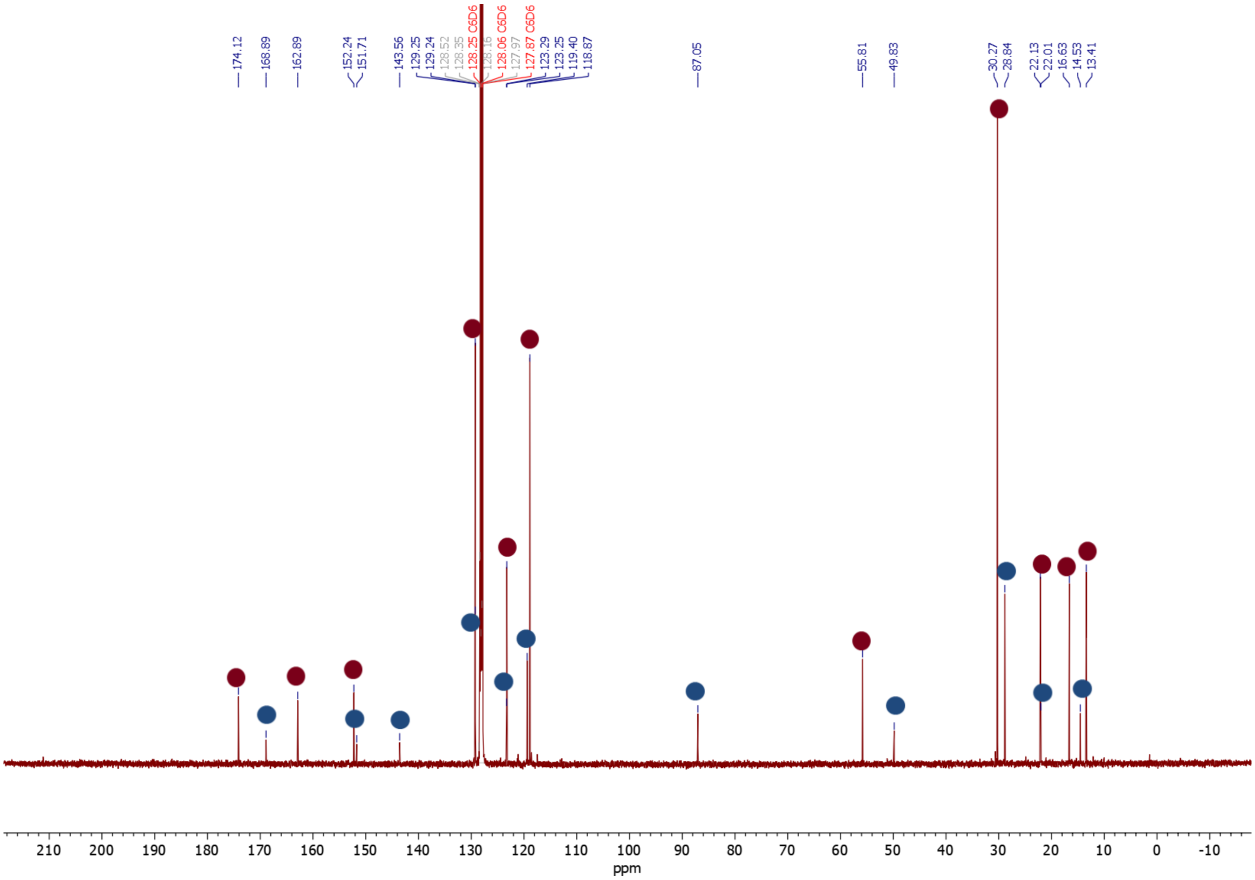
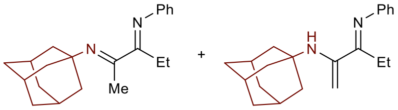


Figure S35. ^{13}C NMR spectrum of **3n** in C_6D_6 (Diimine denoted in red, enamine in blue).

(2E,3E)-N^2-(adamantan-1-yl)-*N*^{3}-phenylpentane-2,3-diimine (**3o)**



Light yellow oil, 43.3 mg. 70% isolated yield of mixture of imine/enamine tautomers in 3.3:1 ratio.

Diimine: ^{1}**H NMR (500 MHz, C_6D_6)** δ 7.21 – 7.16 (m, 1H, CH(C*H*CH)$_2$CN), 6.92 (tt, J = 7.5, 1.3 Hz 1H, C*H*(CHCH)$_2$CN), 6.77 (dd, J = 8.4, 1.3 Hz, 2H, CH(CHC*H*)$_2$CN), 2.71 (q, J = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.30 (s, 3H, C*H*$_3$), 2.04 – 1.98 (m, 3H, NC(CH$_2$)$_3$(C*H*)$_3$(CH$_2$)$_3$), 1.98 – 1.96 (m, 6H, NC(C*H*$_2$)$_3$(CH)$_3$(CH$_2$)$_3$), 1.64 – 1.61 (m, 6H, NC(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$), 1.06 (t, J = 7.5 Hz, 3H, CH$_2$C*H*$_3$). ^{13}**C NMR (126 MHz, C_6D_6)** δ 174.32, 162.11, 152.34, 129.23, 123.22, 118.89, 57.11, 42.95, 36.92, 30.19, 22.20, 17.30, 13.56. **ESI-HRMS (m/z):** calcd. for $C_{15}H_{22}N_2Na^+$, 253.1681; found, 253.1698 (diff. 0.0017).

Enamine: ^{1}**H NMR (500 MHz, C_6D_6)** δ 7.14 – 7.10 (m, 2H, CH(C*H*CH)$_2$CN), 6.89 (t, J = 7.4 Hz, 1H, C*H*(CHCH)$_2$CN), 6.71 – 6.67 (m, 2H, CH(CHC*H*)$_2$CN), 4.73 – 4.60 (m, 2H, C=C*H*$_2$), 2.36 – 2.31 (m, 2H, C*H*$_2$CH$_3$), 1.96 – 1.90 (m, 6H, NC(C*H*$_2$)$_3$(CH)$_3$(CH$_2$)$_3$), 1.87 – 1.79 (m, 3H, NC(CH$_2$)$_3$(C*H*)$_3$(CH$_2$)$_3$), 1.55 – 1.51 (m, 6H, NC(CH$_2$)$_3$(CH)$_3$(C*H*$_2$)$_3$), 0.96 (t, J = 7.6 Hz, 3H, CH$_2$C*H*$_3$). ^{13}**C NMR (126 MHz, C_6D_6)** δ 169.01, 151.80, 142.99, 129.26, 123.26, 119.40, 88.01, 50.78, 42.20, 36.99, 30.08, 21.98, 14.58.

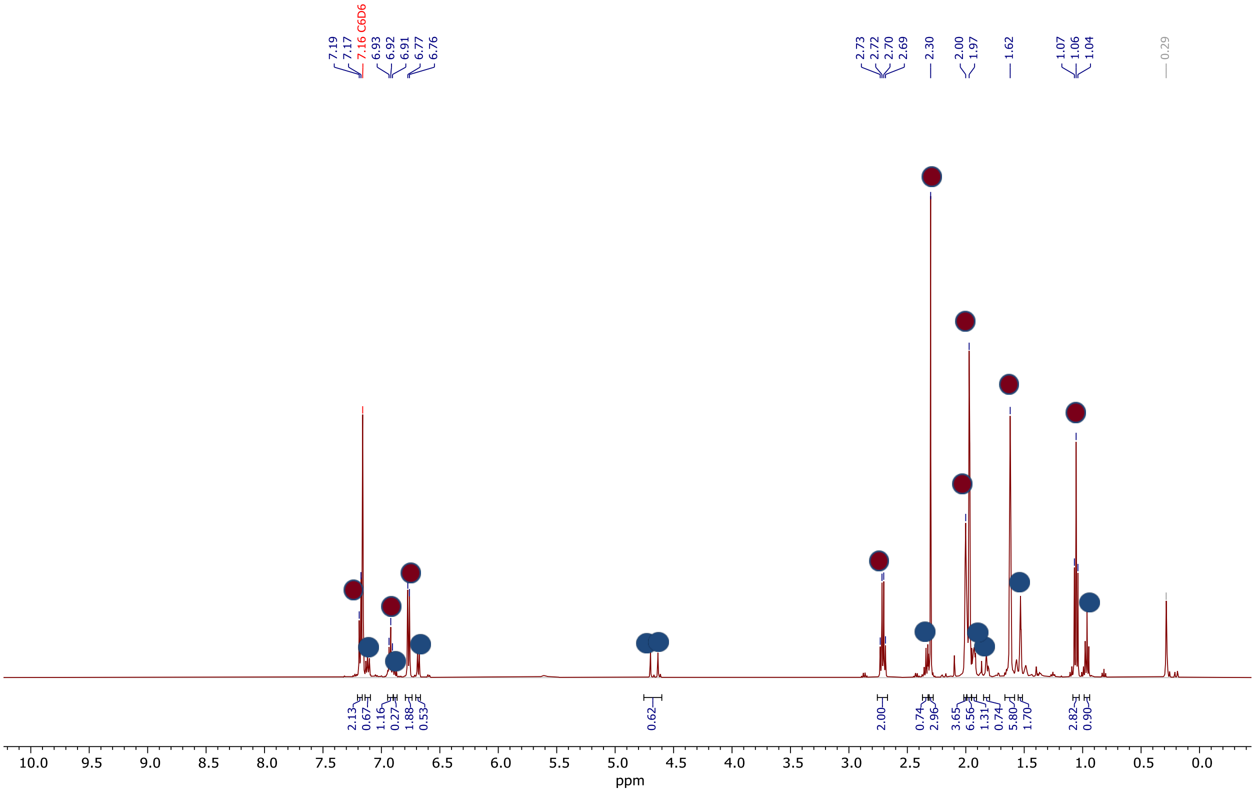


Figure S36. ^{1}H NMR spectrum of **3o** in C_6D_6 (Diimine denoted in red, enamine in blue).

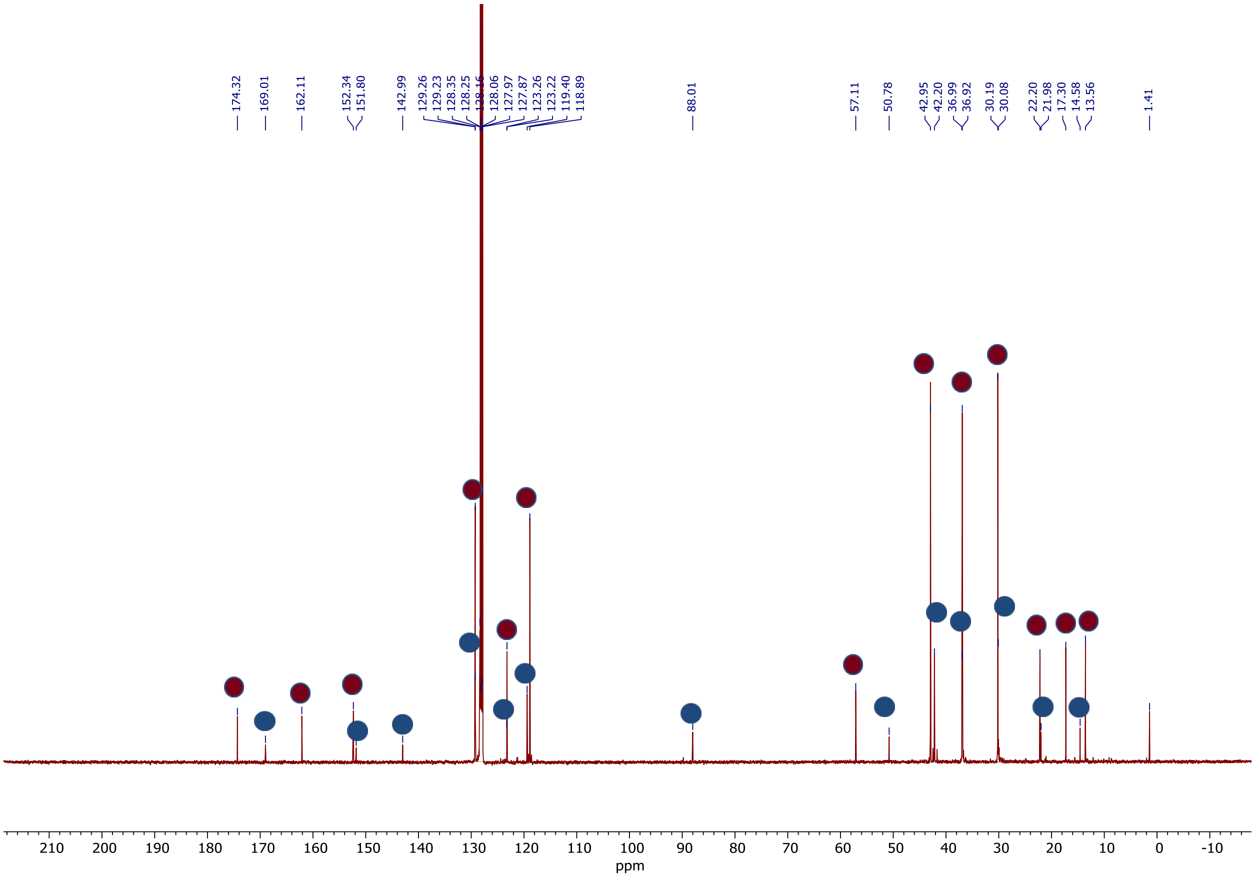
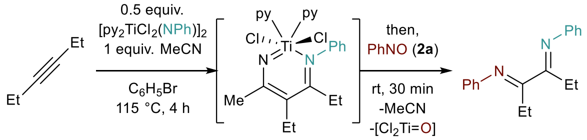


Figure S37. ^{13}C NMR spectrum of **3o** in C_6D_6 (Diimine denoted in red, enamine in blue).

Multicomponent coupling of [py$_2$TiCl$_2$(NPh)]$_2$, 3-hexyne, and acetonitrile with subsequent nitrosobenzene addition for the synthesis of *N*^{2},*N*^{3}-diphenylbutane-2,3-diimine (**5a**) (NMR scale)



Procedure: [py$_2$TiCl$_2$(NPh)]$_2$ (17.0 mg, 0.046 mmol, 1 equiv.), TMB (2.0 mg), and C$_6$D$_5$Br (0.5 mL) were added to an NMR tube, followed by MeCN (2.5 µL, 0.047 mmol) and 3-hexyne (5.3 µL, 0.047 mmol). The tube was capped, sealed with electrical tape, and heated to 115 ˚C in an oil bath for 4 hours. After recording the t = 4 h ^{1}H NMR spectrum, the tube was brought back into the glovebox, where nitrosobenzene (5.0 mg, 0.047 mmol, 1 equiv.) was added. The tube was resealed and a final ^{1}H NMR spectrum was recorded after 30 minutes.

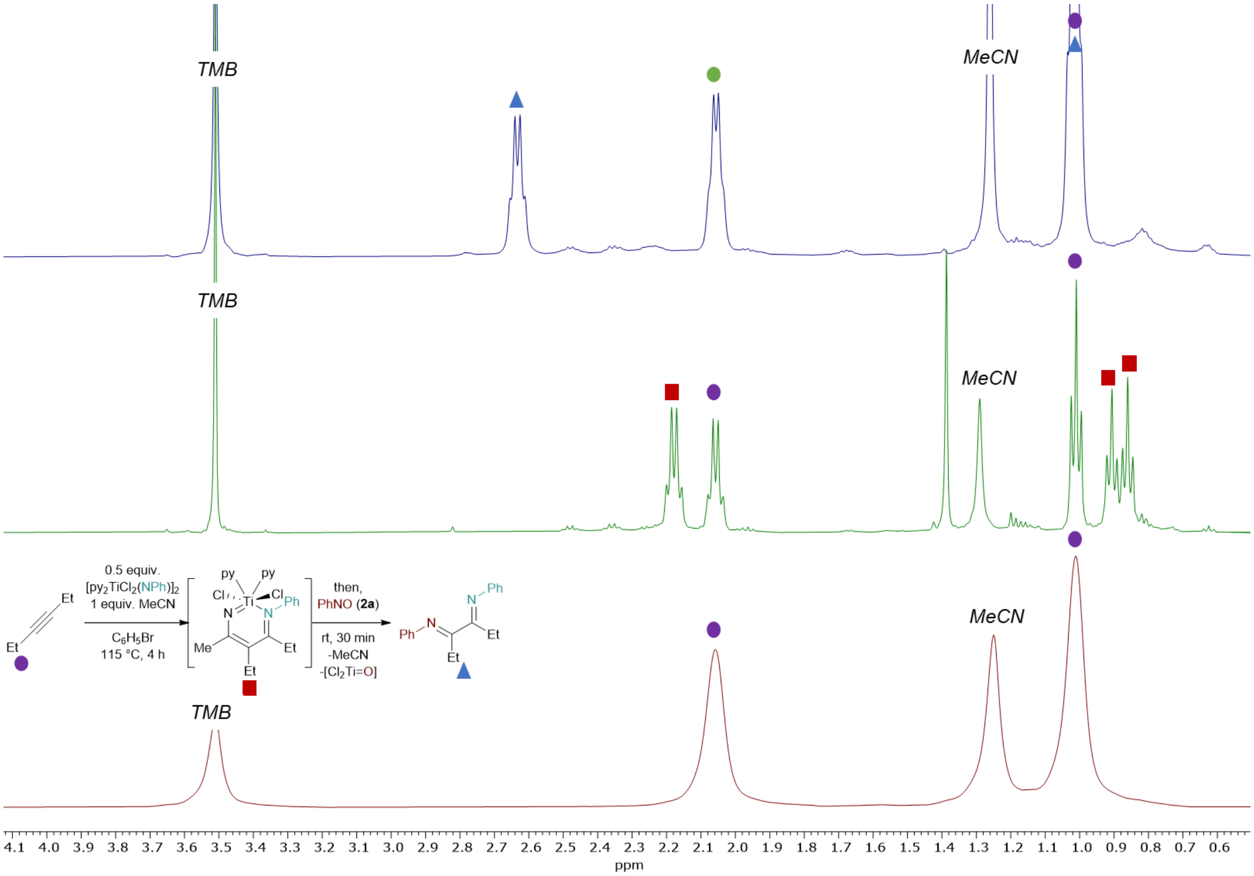


Figure S38. Stacked ^{1}H NMR spectra characterizing the multicomponent coupling of 3-hexyne (1 equiv.), MeCN (1 equiv.) and [py$_2$TiCl$_2$(NPh)]$_2$ in C$_6$D$_5$Br; Bottom (red trace): t = 0; Middle (green trace): t = 4 h at 115 ˚C generating metallacycle **1b** in 54% yield; Top (blue trace): t = 0.5 h after nitrosobenzene addition to give diimine **5b** in 48% yield (90% with respect to **1b**).

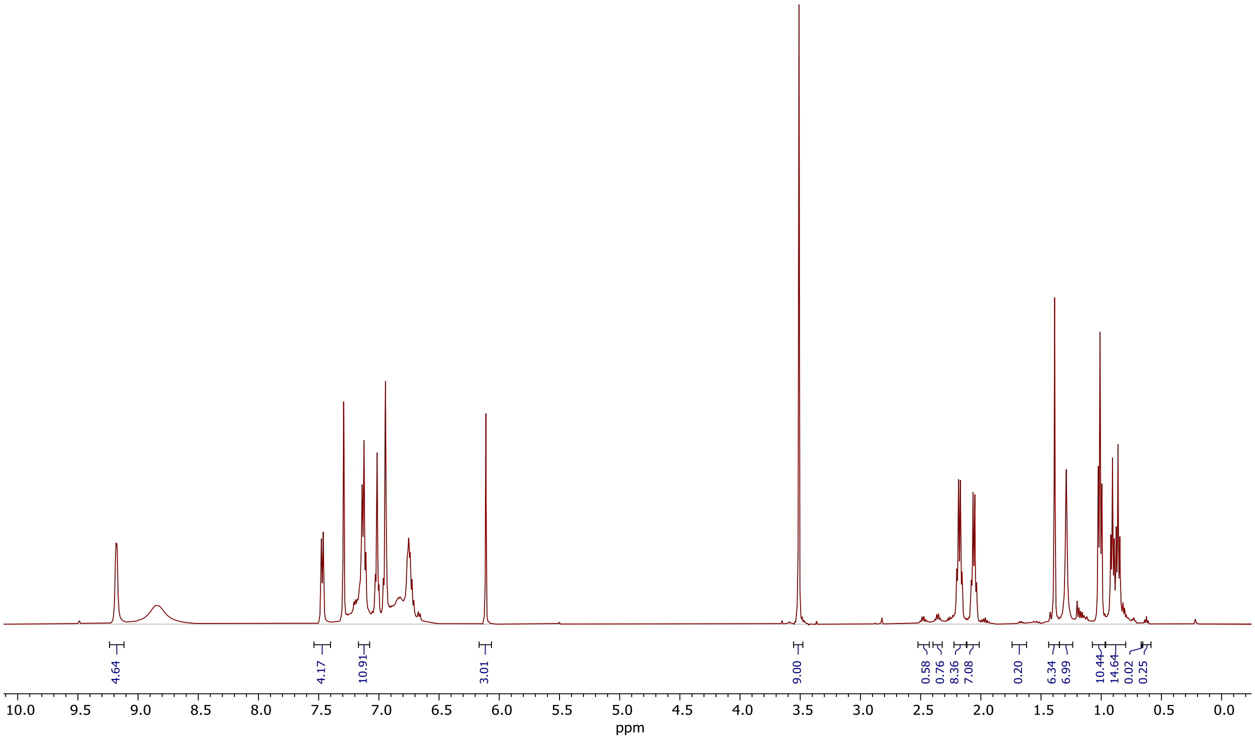


Figure S39. Full unstacked ^{1}H NMR (C_6D_5Br) spectrum (middle trace); t = 4 h at 115 ˚C generating metallacycle **1b** in 54% yield.

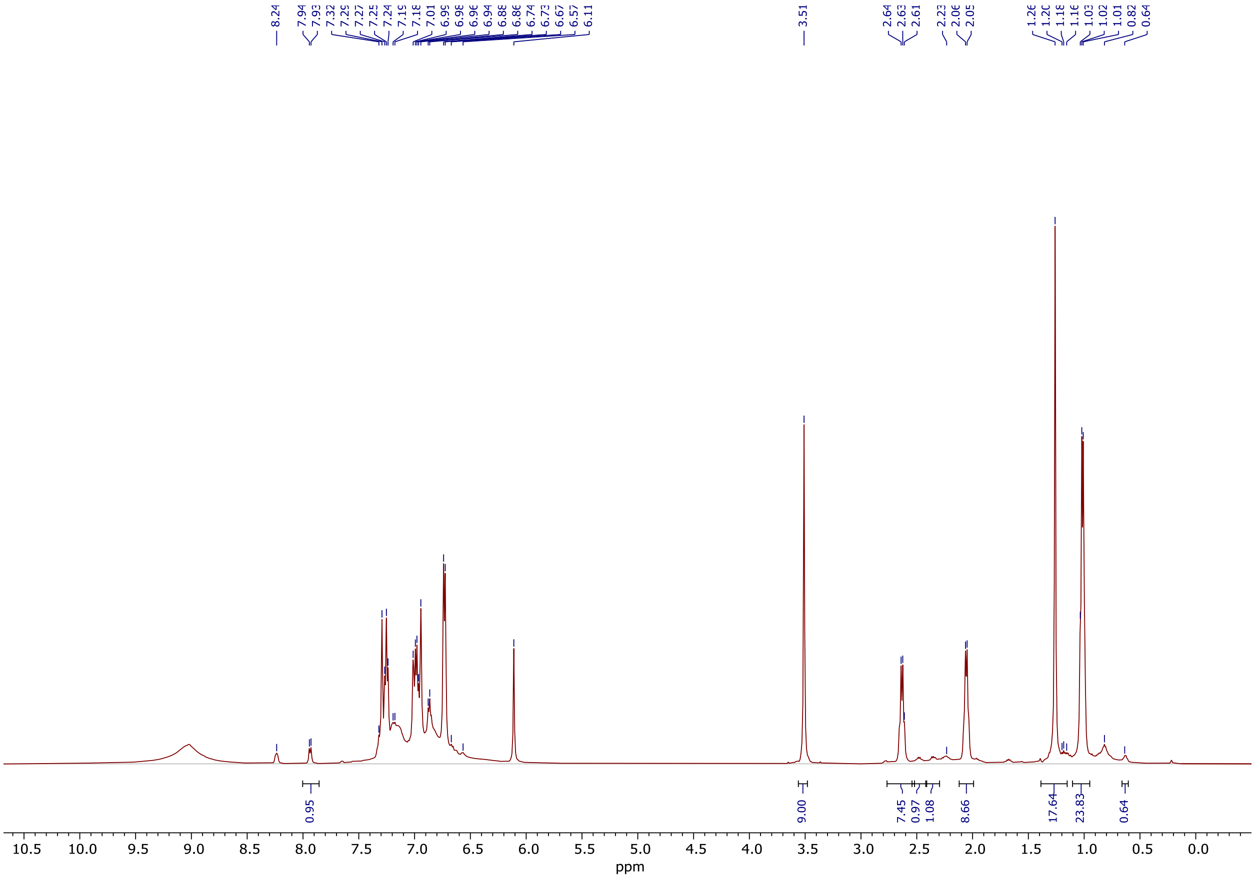
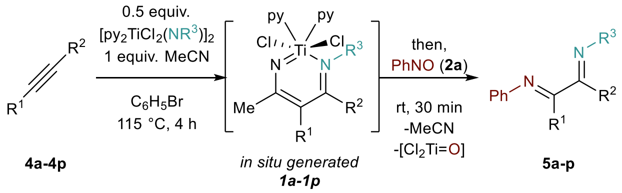


Figure S40. Full unstacked ^{1}H NMR (C_6D_5Br) spectrum (top trace); t = 0.5 h after nitrosobenzene addition to give diimine **5b** in 48% yield (90% with respect to **1b**).

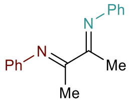
Scope of multicomponent coupling of $[py_2TiCl_2(NPh)]_2$, alkynes, and acetonitrile with subsequent nitrosobenzene addition for the synthesis of α-diimines (isolation scale) (Table 2, **5a – 5p**)



General procedure: $[py_2TiCl_2(NPh)]_2$ (147.2 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 μL, 4.00 mmol, 10 equiv.), and alkyne (0.400 mmol, 1.00 equiv). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 ˚C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na_2CO_3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na_2SO_4, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and, in some cases, volatile alkyne) were reduced under vacuum. Any remaining azobenzene (from the metathesis of leftover imido with nitrosobenzene) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum.

Note on stability: Diimines are highly sensitive to hydrolysis to the corresponding aniline and diketone, and as a result silica/alumina column chromatography was avoided.

(2E,3E)-N^2,N^3-diphenylbutane-2,3-diimine (**5a**)



Dark red solid, 59.8 mg. 63% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.18 (m, 4H, CH(C*H*CH)$_2$CN), 6.95 (t, *J* = 7.5 Hz, 2H, C*H*(CHCH)$_2$CN), 6.73 (d, *J* = 6.9 Hz, 4H, CH(CHC*H*)$_2$CN), 2.11 (s, 6H, C*H$_3$*). **^{13}C NMR (126 MHz, C_6D_6) δ** 168.29, 151.67, 129.28, 124.03, 119.17, 15.27. **ESI-HRMS (m/z):** calcd. for $C_{16}H_{16}N_2Na^+$, 259.1211; found, 259.1208 (diff. 0.0003).

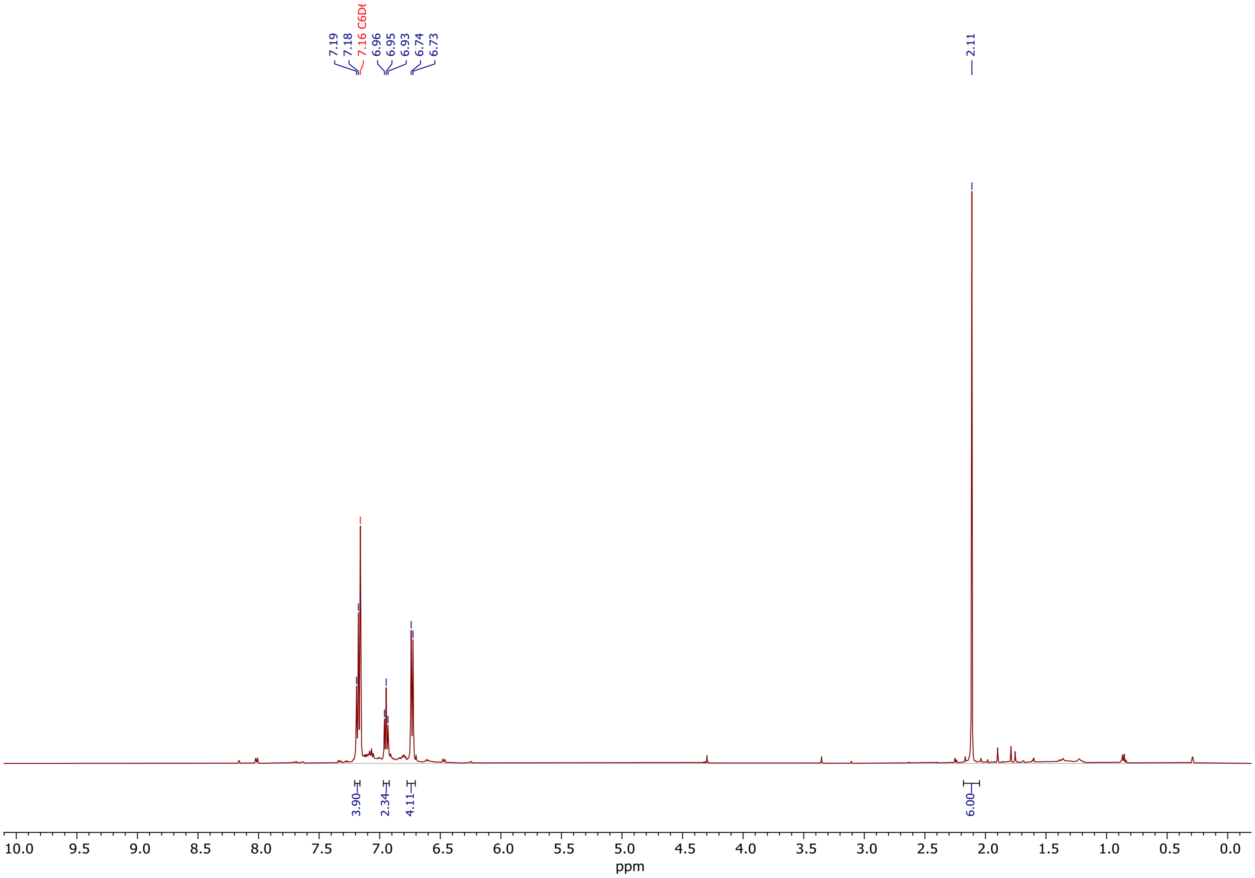


Figure S41. ^{1}H NMR spectrum of **5a** in C_6D_6.

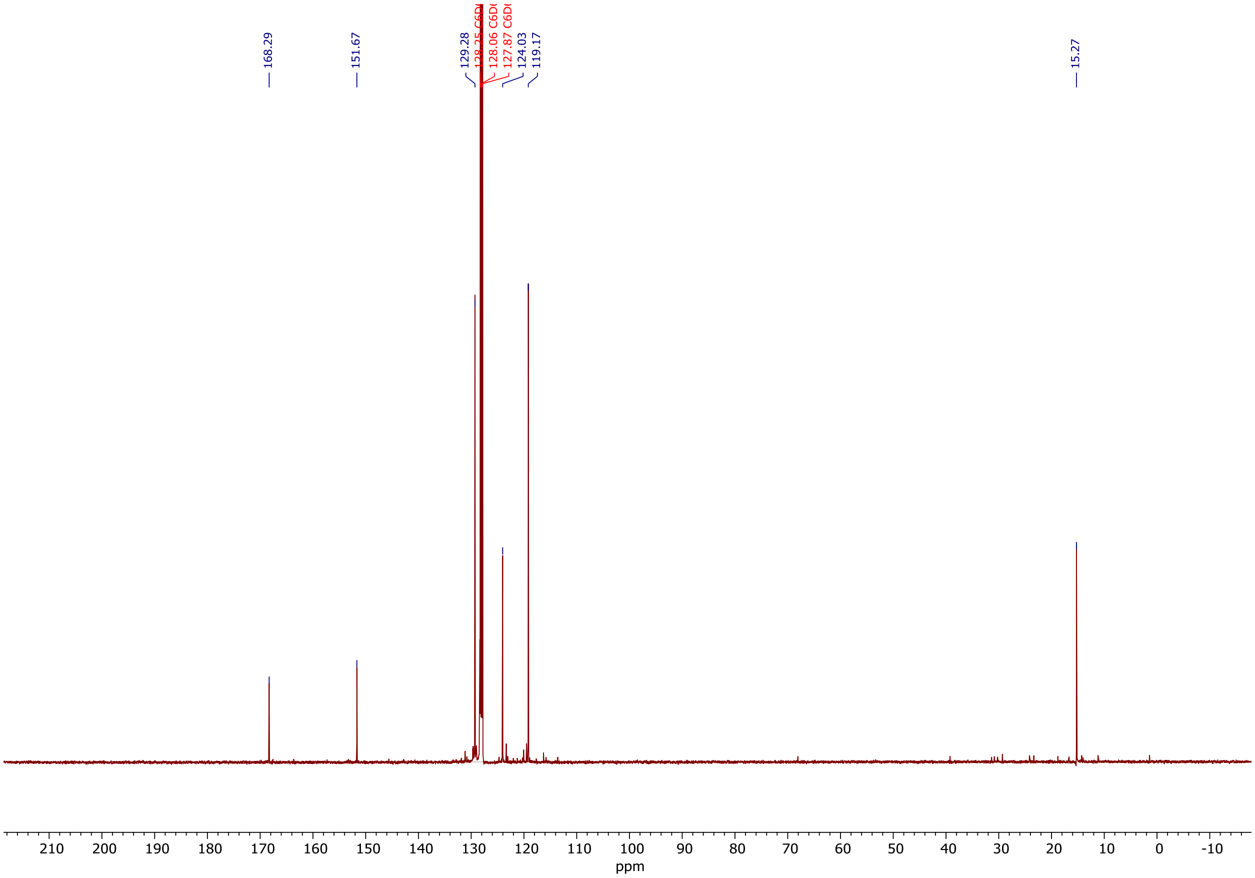
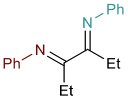


Figure S42. ^{13}C NMR spectrum of **5a** in C_6D_6.

(3E,4E)-N^3,*N*^{4}-diphenylhexane-3,4-diimine (**5b**)



Red oil, 60.3 mg. 57% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.24 – 7.16 (m, 4H, CH(C*H*CH)$_2$CN), 6.94 (t, *J* = 7.5 Hz, 2H, C*H*(CHCH)$_2$CN), 6.74 (dd, *J* = 8.3, 1.3 Hz, 4H, CH(CHC*H*)$_2$CN), 2.70 (q, *J* = 7.5 Hz, 4H, C*H*$_2$CH$_3$), 1.04 (t, *J* = 7.5 Hz, 6H, CH$_2$C*H*$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 171.66, 151.52, 129.29, 123.71, 118.73, 22.12, 12.90. **ESI-HRMS (m/z):** calcd. for $C_{18}H_{20}N_2Na^+$, 287.1524; found, 287.1525 (diff. 0.0001).

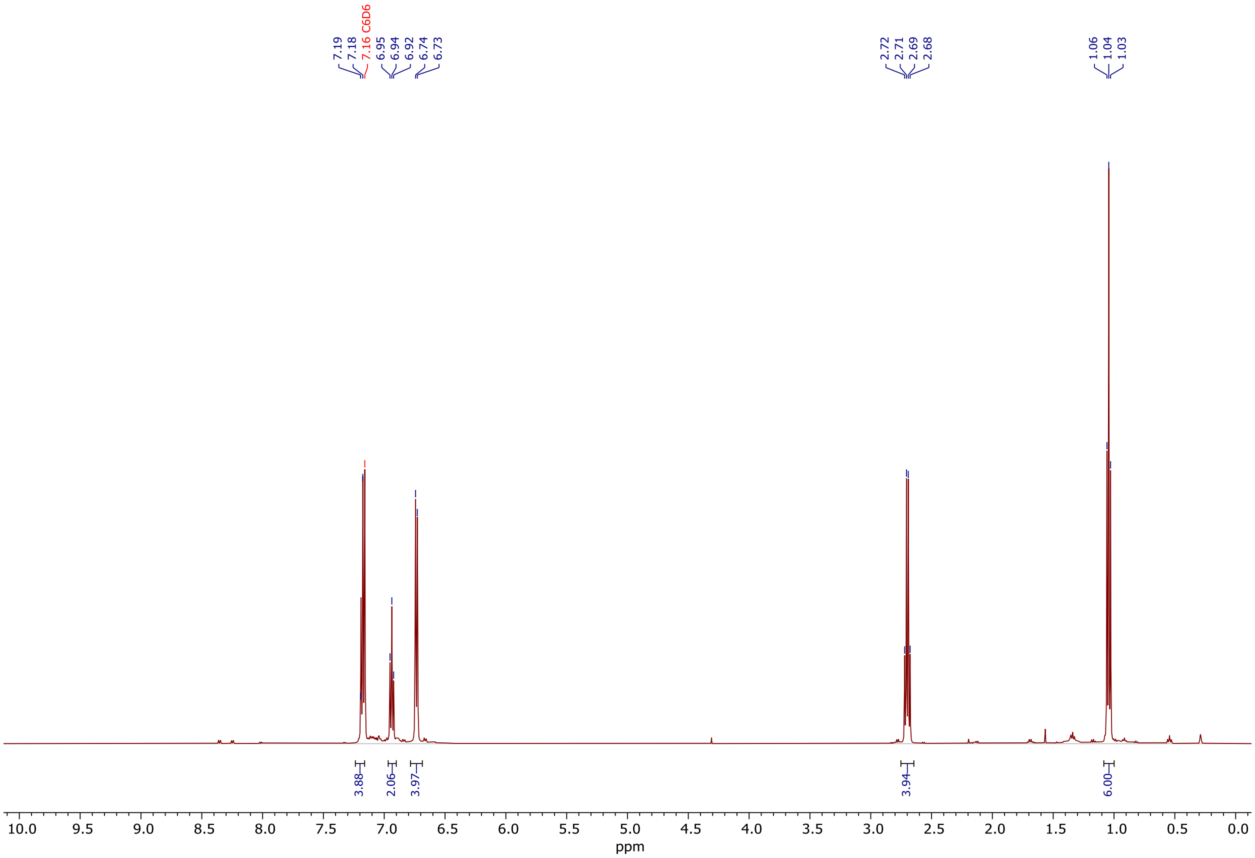


Figure S43. ^{1}H NMR spectrum of **5b** in C_6D_6.

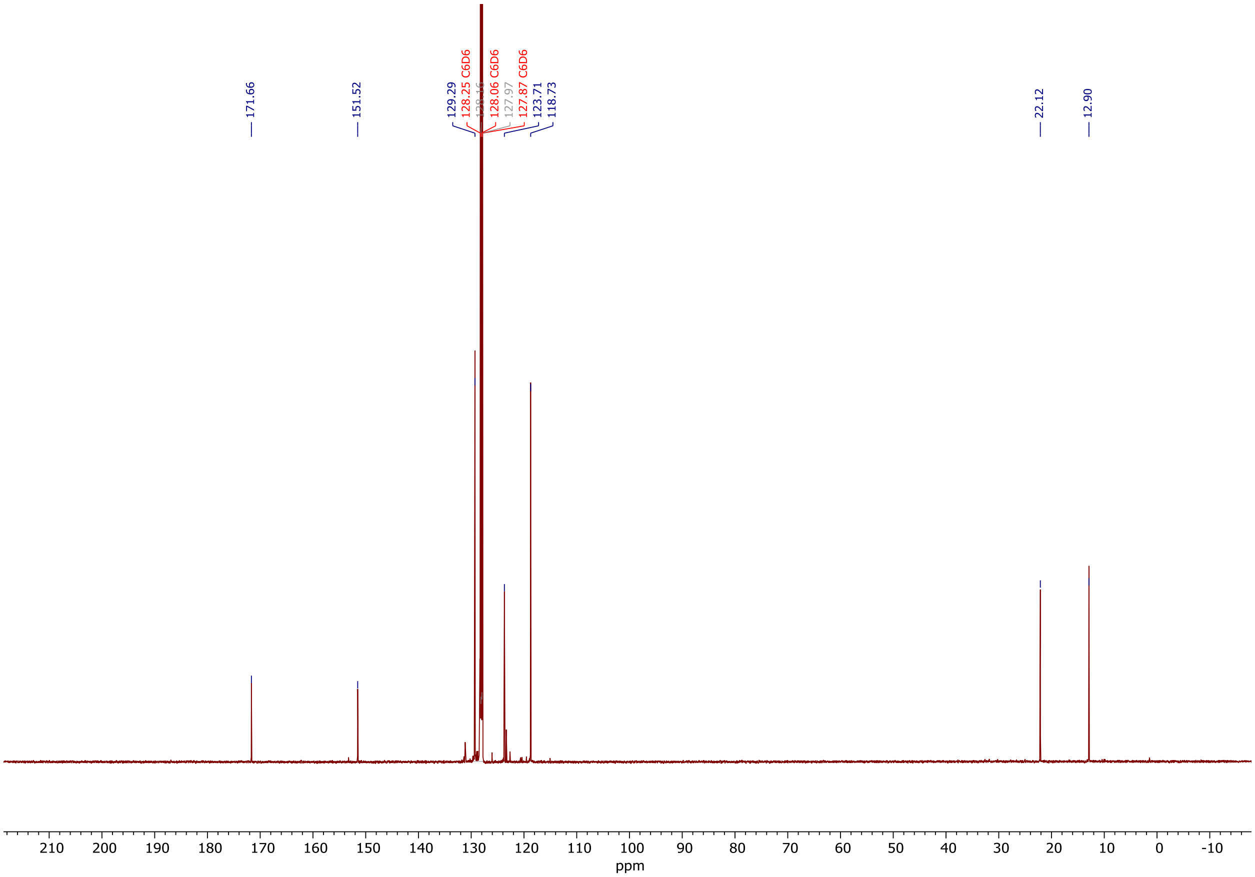
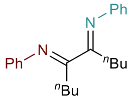


Figure S44. ^{13}C NMR spectrum of **5b** in C_6D_6.

(5E,6E)-*N*^{5},*N*^{6}-diphenyldecane-5,6-diimine (**5c**)



Red solid, 59.9 mg. 51% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.18 (d, *J* = 7.4 Hz, 2H, CH(C*H*CH)$_2$CN), 6.93 (tt, *J* = 7.3, 1.2 Hz, 2H, C*H*(CHCH)$_2$CN), 6.78 (d, *J* = 8.3 Hz, 2H, CH(CHC*H*)$_2$CN), 2.84 – 2.78 (m, 4H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.61 (p, *J* = 7.8 Hz, 4H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.18 (h, *J* = 7.4 Hz, 4H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.74 (t, *J* = 7.3 Hz, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$). **^{13}C NMR (101 MHz, C_6D_6)** δ 171.14, 151.58, 129.25, 123.71, 118.82, 30.67, 28.44, 23.21, 13.91, 1.42. **ESI-HRMS (m/z):** calcd. for $C_{22}H_{28}N_2Na^+$, 343.2150; found, 343.2164. (diff. 0.0014).

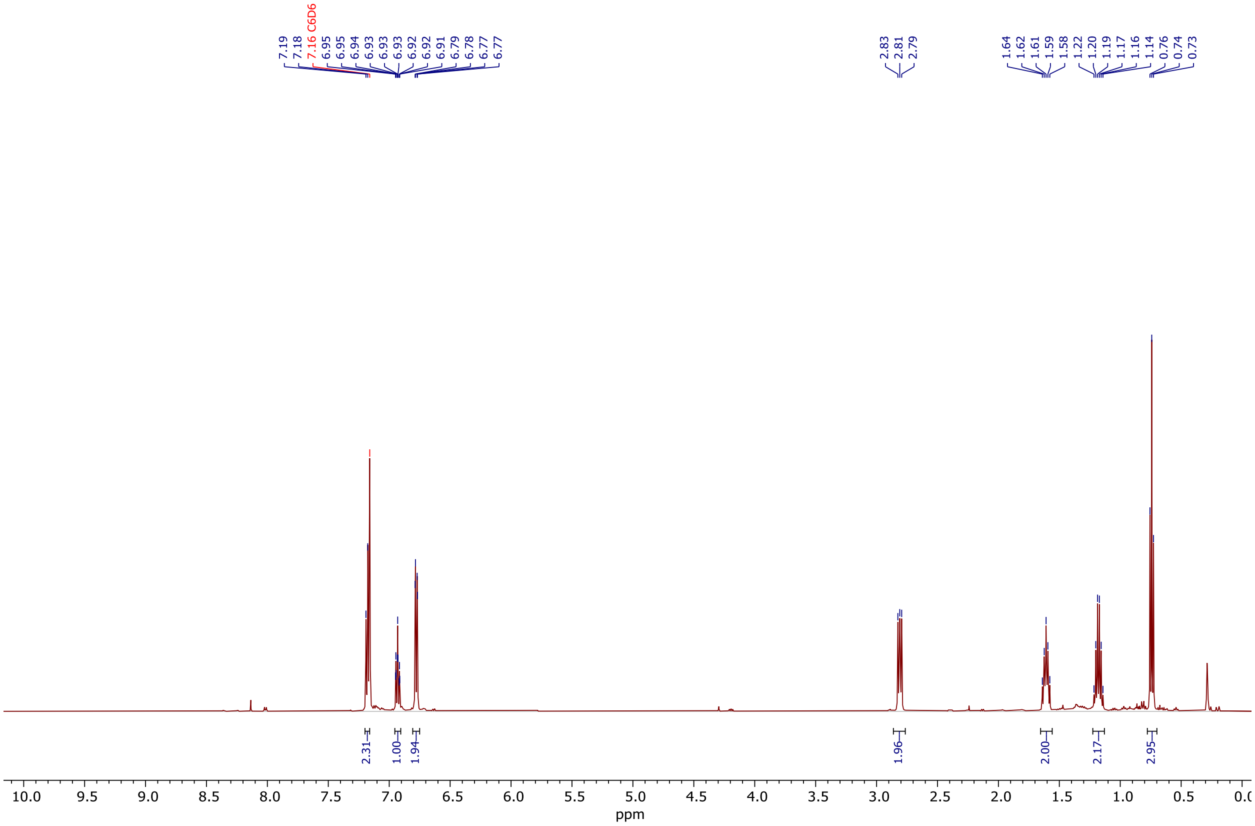


Figure S45. ^{1}H NMR spectrum of **5c** in C_6D_6.

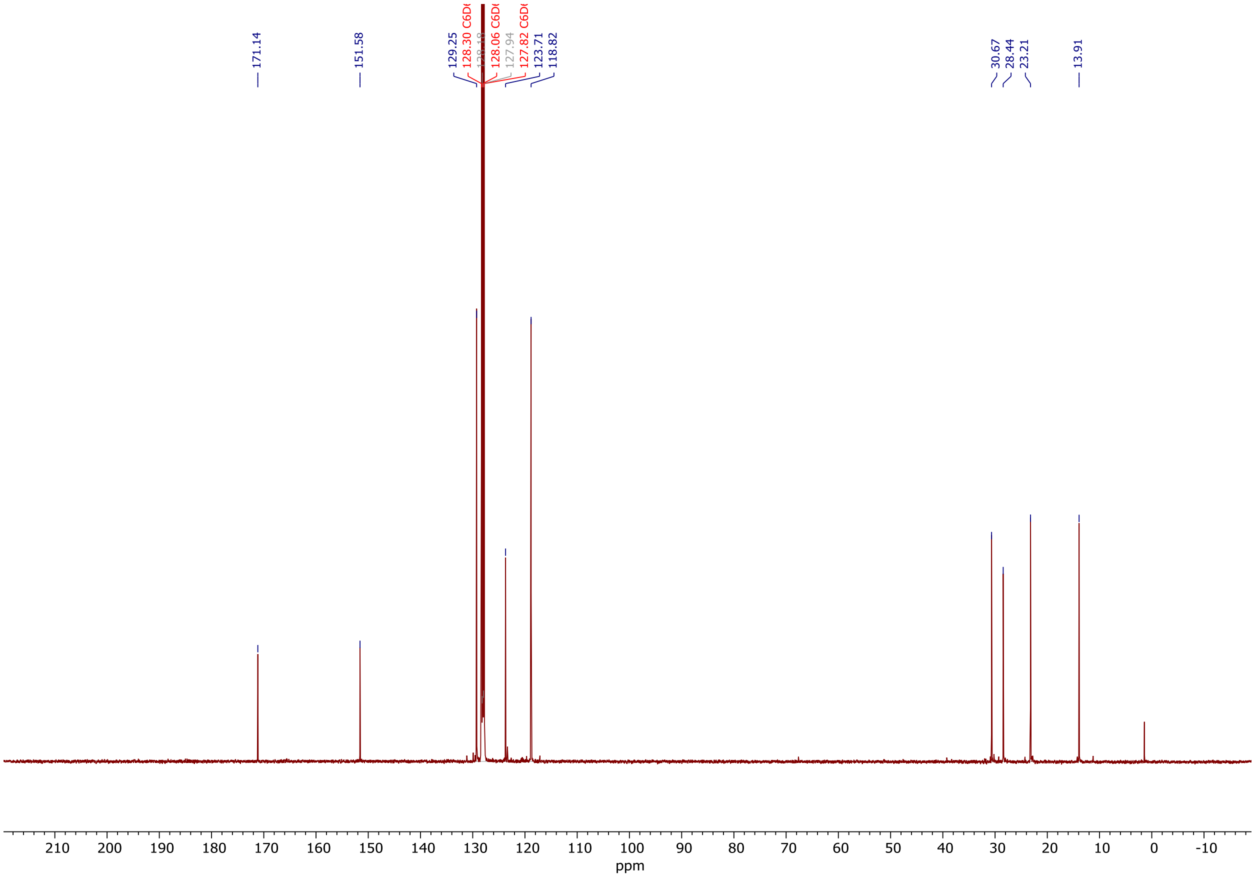
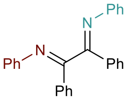


Figure S46. ^{13}C NMR spectrum of **5c** in C_6D_6.

(1E,2E)-N^1,N^2-1,2-tetraphenylethane-1,2-diimine (**5d**)



Light brown solid, 80.8 mg. 56% isolated yield using conditions A, 35% yield using conditions B (see below). **^{1}H NMR (500 MHz, C_6D_6)** δ 8.11 – 8.03 (m, 4H, CH(CHC*H*)$_2$CC), 7.07 – 6.99 (m, 6H, CH(C*H*CH)$_2$CC & C*H*(CHCH)$_2$CC), 6.92 – 6.88 (m, 4H, CH(C*H*CH)$_2$CN), 6.81 (d, *J* = 7.6 Hz, 6H, CH(CHC*H*)$_2$CN & C*H*(CHCH)$_2$CN). **^{13}C NMR (126 MHz, C_6D_6)** δ 164.17, 150.19, 138.36, 131.25, 128.98, 128.80, 128.73, 125.17, 120.69. **ESI-HRMS (m/z):** calcd. for $C_{26}H_{20}N_2Na^+$, 383.1524; found, 383.1512. (diff. 0.0012).

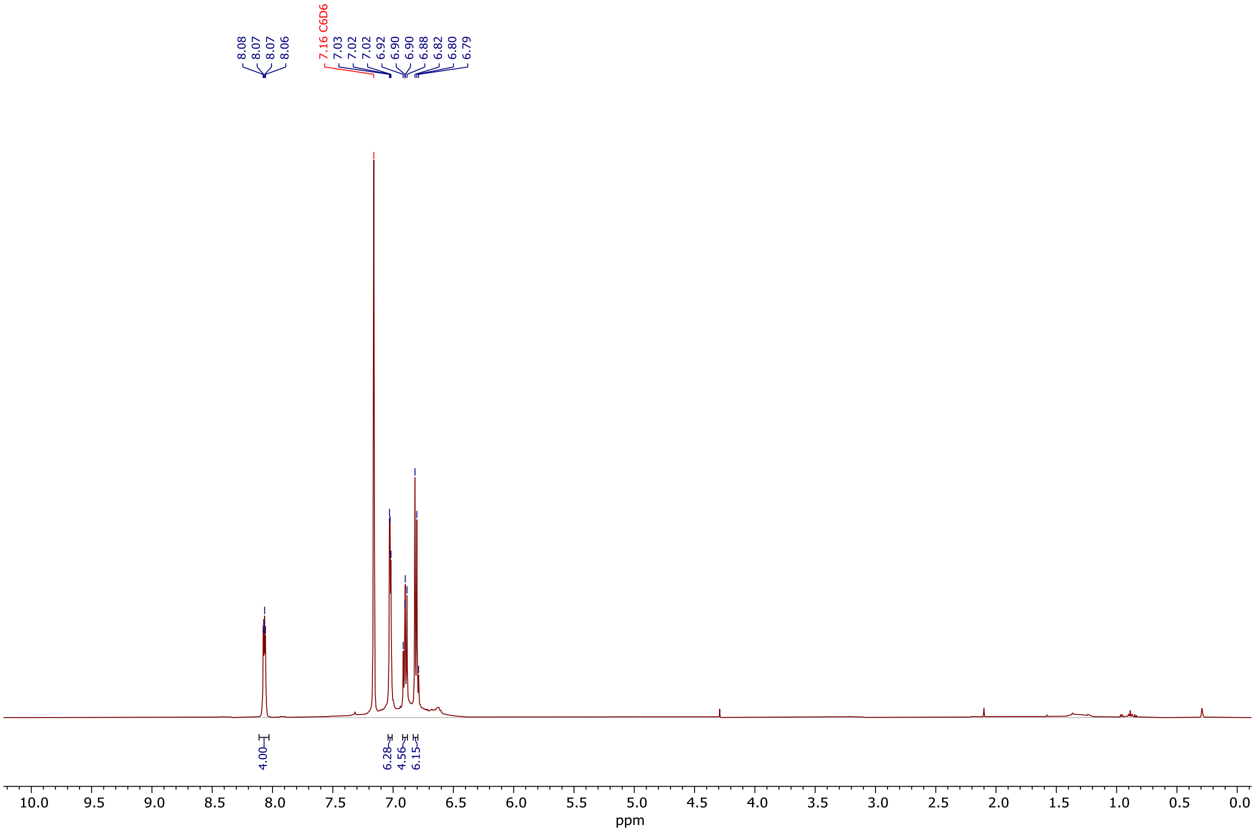


Figure S47. ^{1}H NMR spectrum of **5d** in C_6D_6.

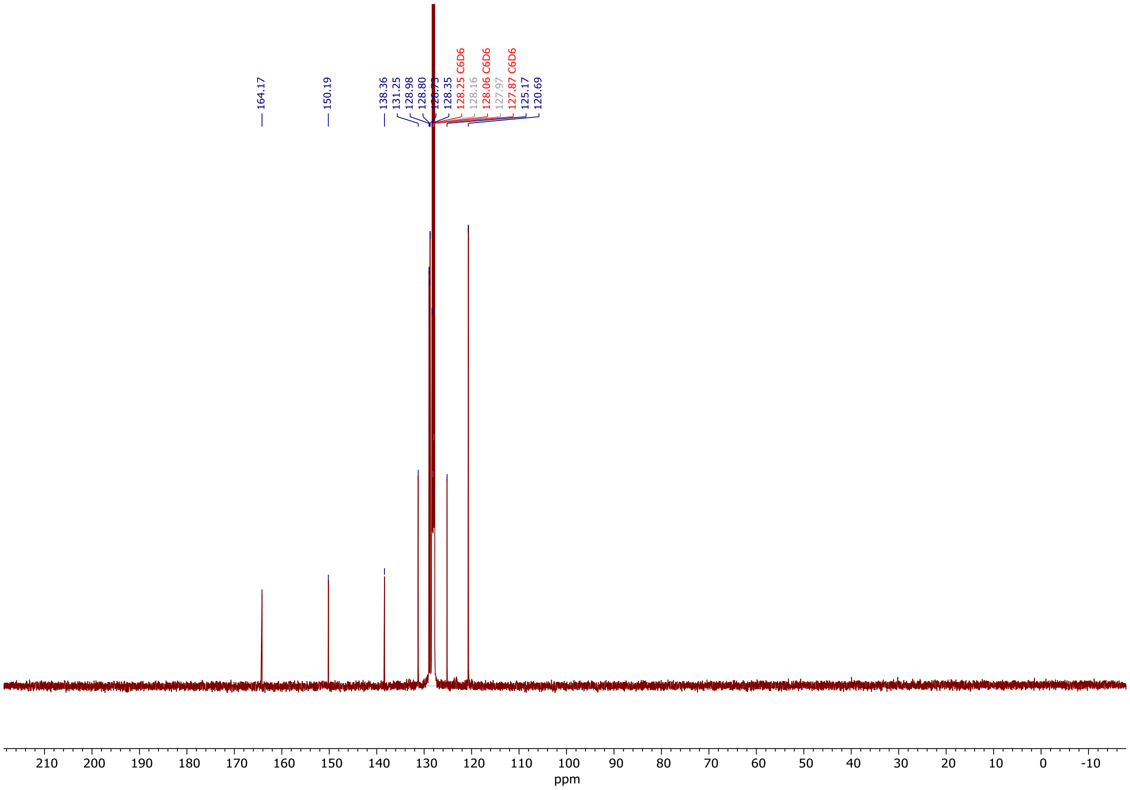
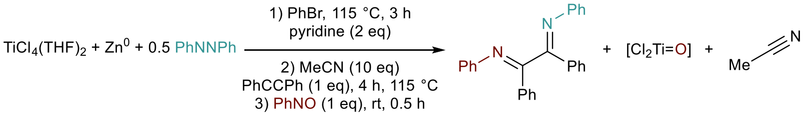


Figure S48. ^{13}C NMR spectrum of **5d** in C_6D_6.

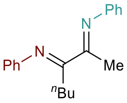
Synthesis of ***5d*** using alternative method from *in-situ* imido generation using $TiCl_4(THF)_2$, Zn^0, and azobenzene



Procedure for synthesis of 5d using *conditions b*: $TiCl_4(THF)_2$ (133.6 mg, 0.400 mmol, 1 equiv.), Zn^0 (65.4 mg, 0.48 mmol, 1.2 equiv.), and azobenzene (36.5 mg, 0.2 mmol, 0.5 equiv.), PhBr (4 mL), pyridine (64.4 µL, 0.8 mmol, 2 equiv.) and a stir bar were added to a 20 mL scintillation vial. The vial was heated for 3 hours at 115 °C. After allowing the vial to cool to room temperature, acetonitrile (208 µL, 4.00 mmol, 10 equiv.), and diphenylacetylene **4d** (0.400 mmol, 1.00 equiv.) were added. The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 ˚C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene **2a** (42.8 mg, 0.4 mmol, 1 equiv.) was added. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na_2CO_3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na_2SO_4, and filtered. The volatiles (including bromobenzene, DCM, MeCN) were reduced under vacuum. Any remaining azobenzene (from the metathesis of leftover imido with nitrosobenzene) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum.

Any remaining diphenylacetylene was also be removed by prolonged heating under vacuum. Diimine **5d** was obtained with a 35% yield using this alternative method (50.4 mg).

(2E,3E)-N^2,*N*^{3}-diphenylheptane-2,3-diimine (**5e**)



Red oil, 58.3 mg. 52% isolated yield. **^{1}H NMR (500 MHz, C$_6$D$_6$)** δ 7.23 – 7.13 (m, 4H, CH(C*H*CH)$_2$CNC(CH$_2$)$_3$CH$_3$ & CH(C*H*CH)$_2$CNCCH$_3$), 7.00 – 6.85 (m, 2H, C*H*(CHCH)$_2$CNC(CH$_2$)$_3$CH$_3$ & C*H*(CHCH)$_2$CNCCH$_3$), 6.82 – 6.76 (m, 2H, CH(CHC*H*)$_2$CNC(CH$_2$)$_3$CH$_3$), 6.75 – 6.69 (m, 2H, CH(CHC*H*)$_2$CNCCH$_3$), 2.83 – 2.75 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.13 (s, 3H, C*H*$_3$), 1.59 (p, *J* = 7.8 Hz, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.16 (h, *J* = 7.4 Hz, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.73 (t, *J* = 7.4 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$). **^{13}C NMR (101 MHz, C$_6$D$_6$)** δ 171.87, 167.57, 151.64, 151.61, 129.30, 129.24, 124.00, 123.74, 119.11, 118.84, 30.90, 28.35, 23.26, 15.66, 13.92. **ESI-HRMS (m/z):** calcd. for $C_{19}H_{22}N_2Na^+$, 301.1681; found, 301.1690. (diff. 0.0009).

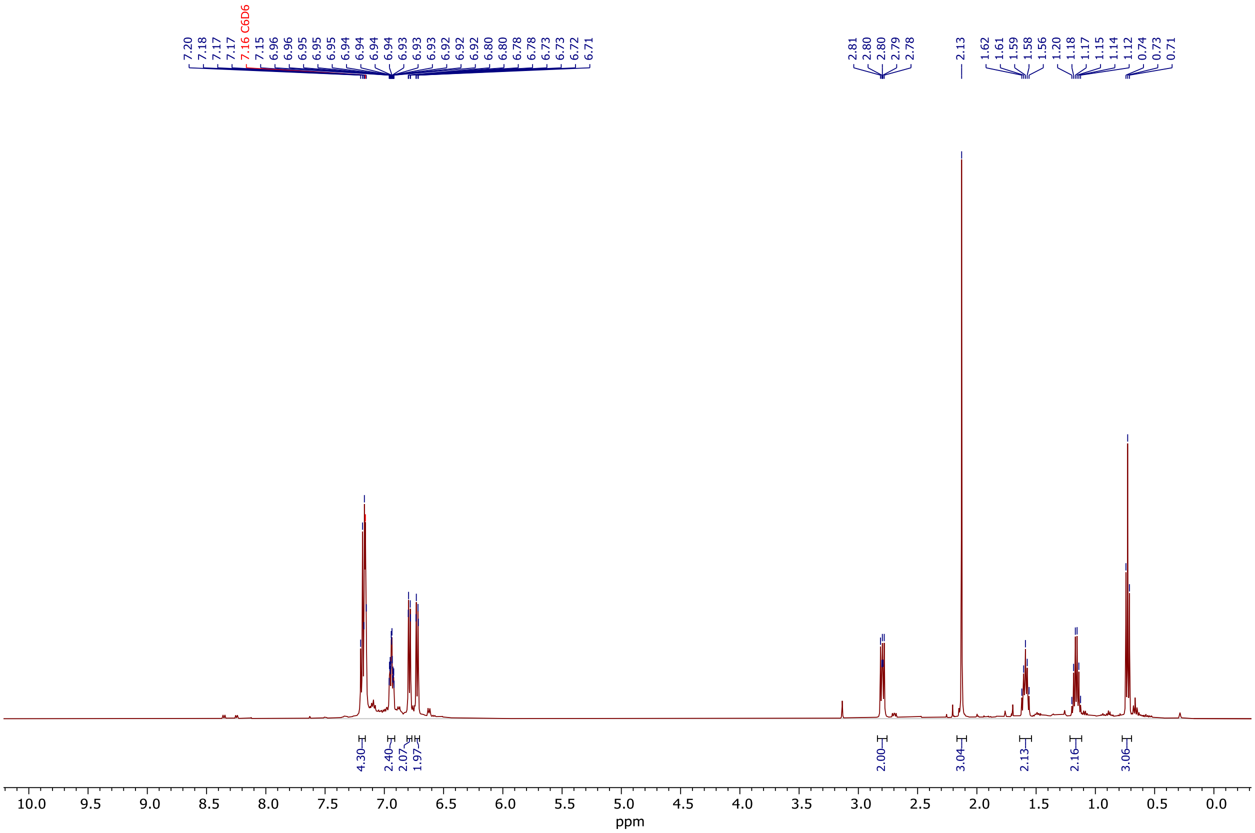


Figure S49. ^{1}H NMR spectrum of **5e** in C$_6$D$_6$.

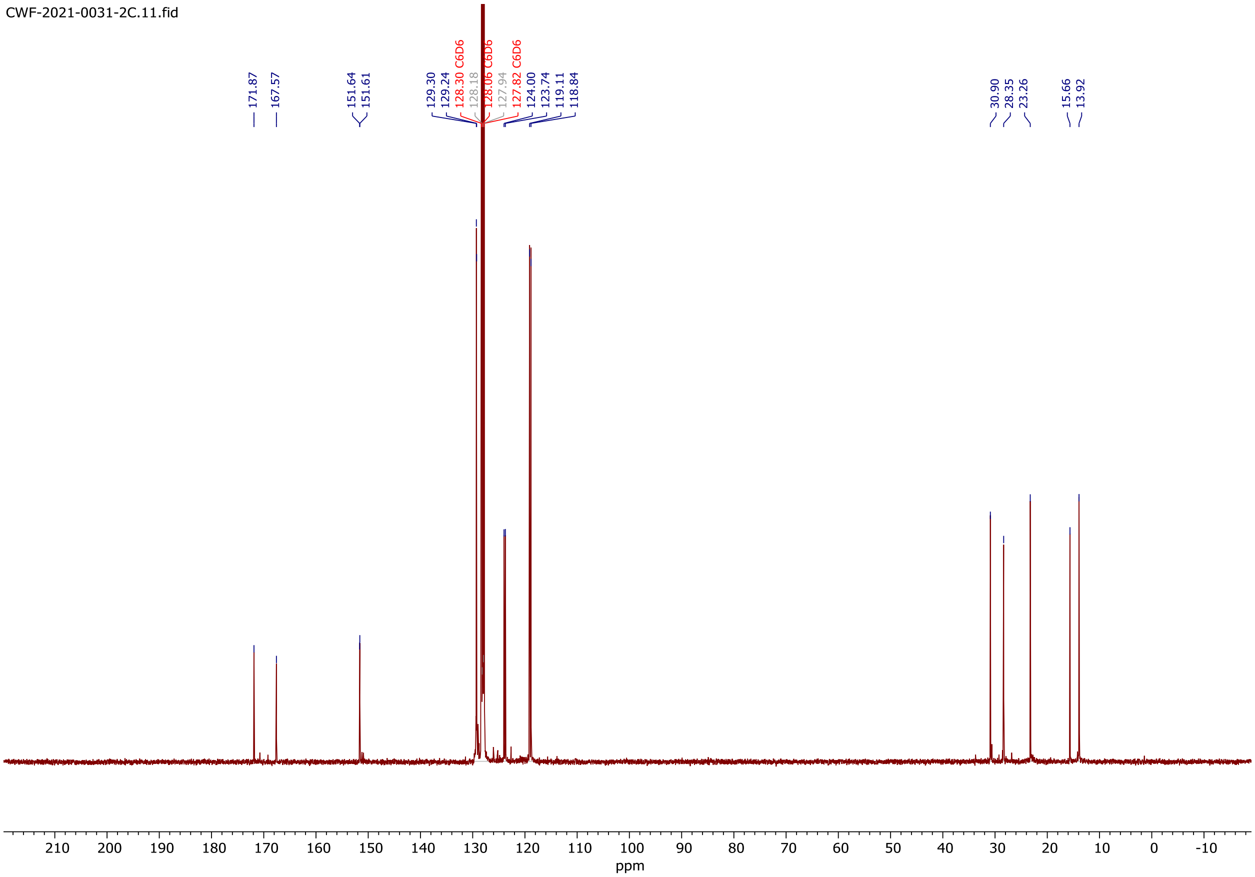
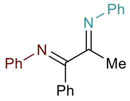
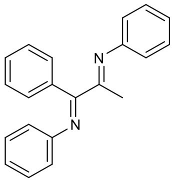


Figure S50. ^{13}C NMR spectrum of **5e** in C_6D_6.

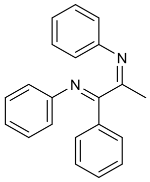
N^1,*N^2*-1-triphenylpropane-1,2-diimine (**5f**)



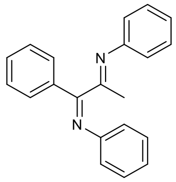
Brown oil, 67.5 mg. 57% isolated yield in a mixture of three isomers in a 3.2:1.8:1 ratio. **ESI-HRMS (m/z):** calcd. for $C_{21}H_{18}N_2Na^+$, 321.1368; found, 321.1352. (diff. 0.0016).



(1*E*,2*E*)-*N^1*,*N^2*,1-triphenylpropane-1,2-diimine



(1E,2Z)-N_1,N_2,1-triphenylpropane-1,2-diimine



(1Z,2E)-N_1,N_2,1-triphenylpropane-1,2-diimine

The major isomer is likely to be E,E, and based on chemical shift arguments and DFT NMR Gauge-Independent Atomic Orbital (GIAO) calculations,[10] Minor Isomer A and Minor Isomer B are tentatively assigned to be Z,E and E,Z, respectively.

The aryl region from 7.25 to 6.75 ppm in the ^{1}H NMR is too highly overlapped to be confidently assigned.

^{1}H NMR (500 MHz, C_6D_6) δ 8.27 – 8.17 (m, 2H, Major Isomer), 7.96 – 7.85 (m, 1H, Minor Isomer B), 7.26 – 7.19 (m, 3H), 7.18 (d, *J* = 1.6 Hz, 1H), 7.15 – 7.07 (m, 8H), 7.07 – 7.04 (m, 1H), 7.03 – 6.83 (m, 7H), 6.83 – 6.76 (m, 3H), 6.72 – 6.67 (m, 1H, Minor Isomer B), 6.67 – 6.63 (m, 1H, Minor Isomer A), 6.63 – 6.59 (m, 2H, Major Isomer), 2.28 (s, 2H, Minor Isomer A), 2.15 (s, 1H, Minor Isomer B), 1.43 (s, 3H, Major Isomer).

Major Isomer (E,E): **^{13}C NMR (126 MHz, C_6D_6)** δ 167.28, 167.05, 151.35, 150.25, 136.43, 131.39, 130.31, 129.35, 129.17, 128.90, 128.87, 128.82, 120.93, 119.50, 20.16.

Minor Isomer A (Z,E): **^{13}C NMR (126 MHz, C_6D_6)** δ 168.52, 168.48, 151.64, 150.86, 135.24, 128.94, 128.88, 128.76, 128.35, 127.62, 124.24, 124.17, 121.01, 118.96, 16.28.

Minor Isomer B (E,Z): **^{13}C NMR (126 MHz, C_6D_6)** δ 166.11, 165.29, 150.59, 149.89, 136.61, 131.30, 128.97, 128.57, 125.07, 124.85, 124.21, 124.00, 120.78, 120.10, 27.90.

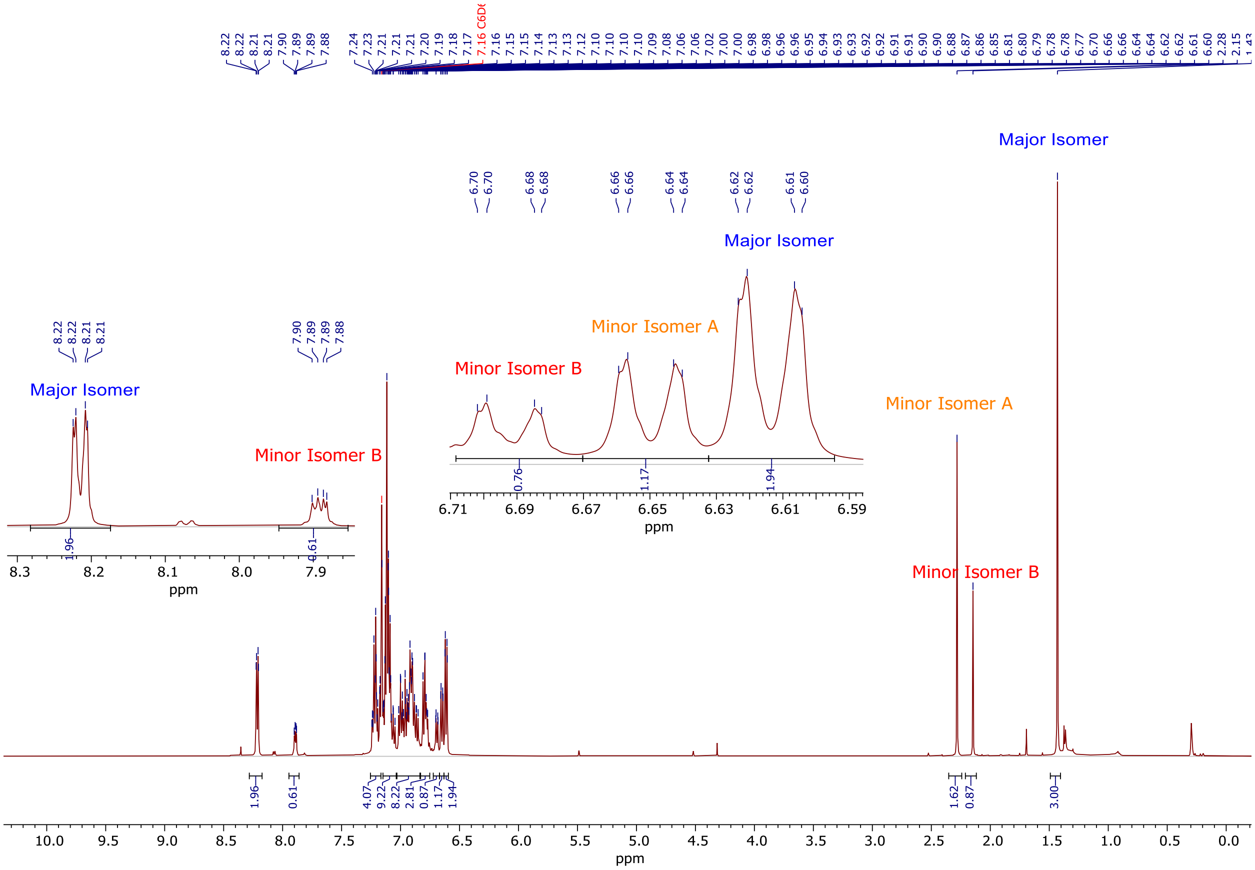


Figure S51. ^{1}H NMR spectrum of **5f** as a mixture of isomers in C_6D_6.

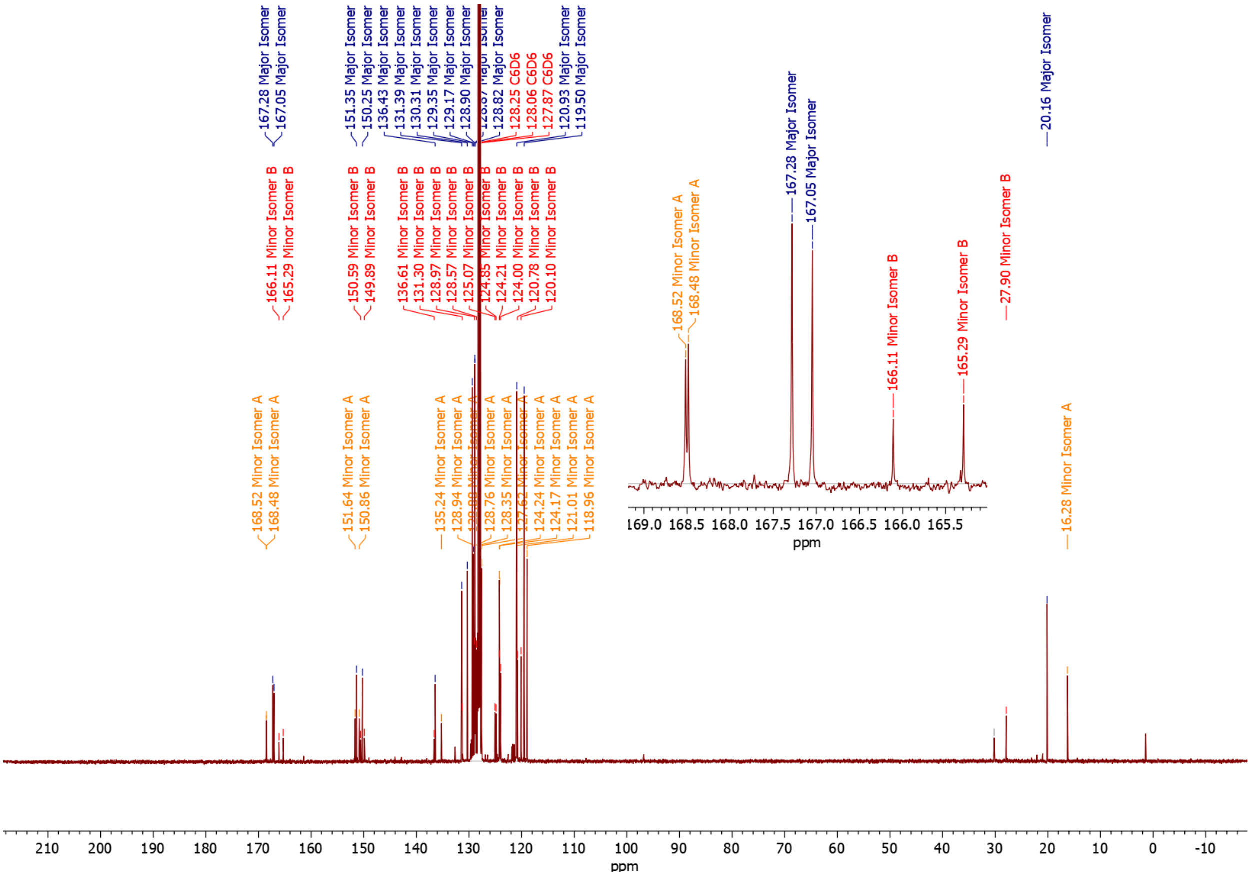


Figure S52. ^{13}C NMR spectrum of **5f** as a mixture of isomers in C_6D_6, with inset showing the imine region.

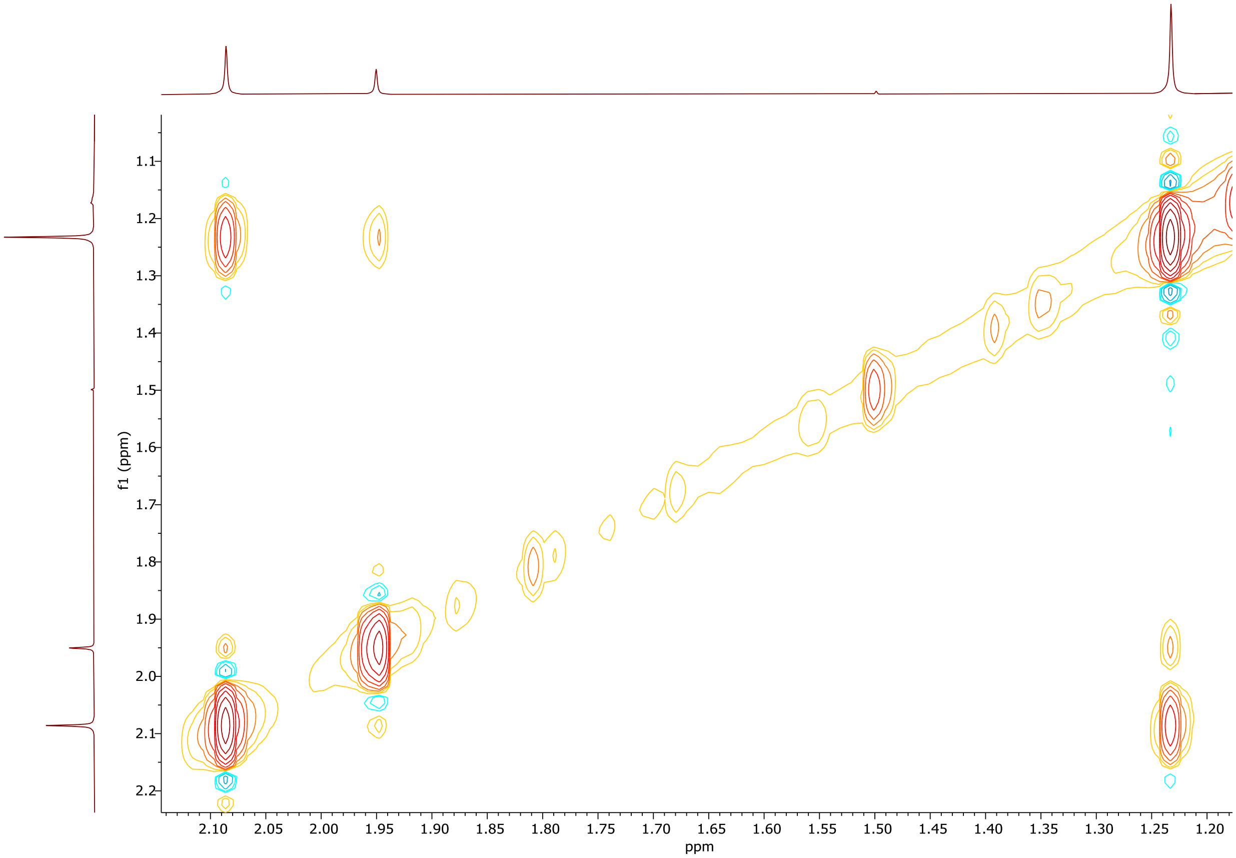


Figure S53. NOESY of methyl region (1.20 – 2.10 ppm) of **5f** showing EXSY cross-peaks that indicate chemical exchange between different diimine isomers, as opposed to through-space interactions (NOEY); EXSY cross-peaks = same phase as diagonal, NOESY = opposite phase.

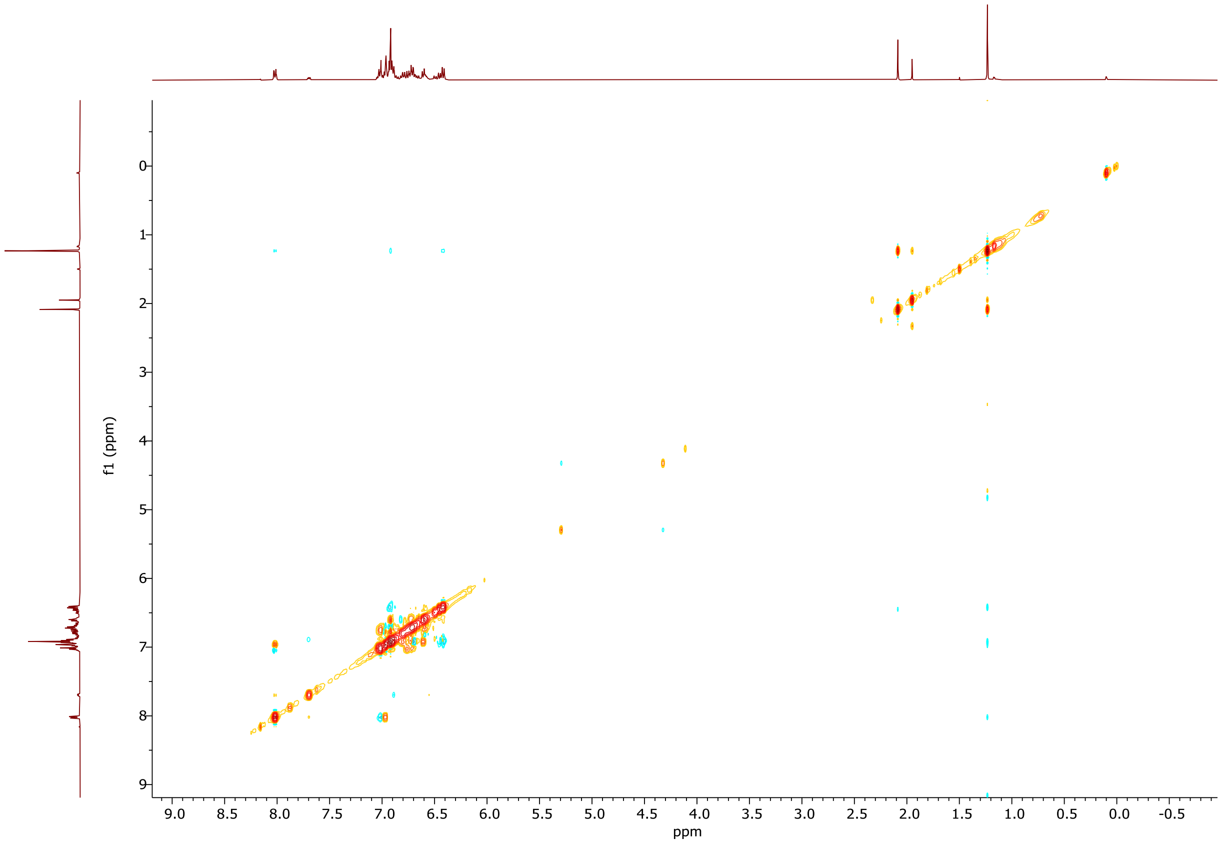


Figure S54. Full NOESY of **5f.**

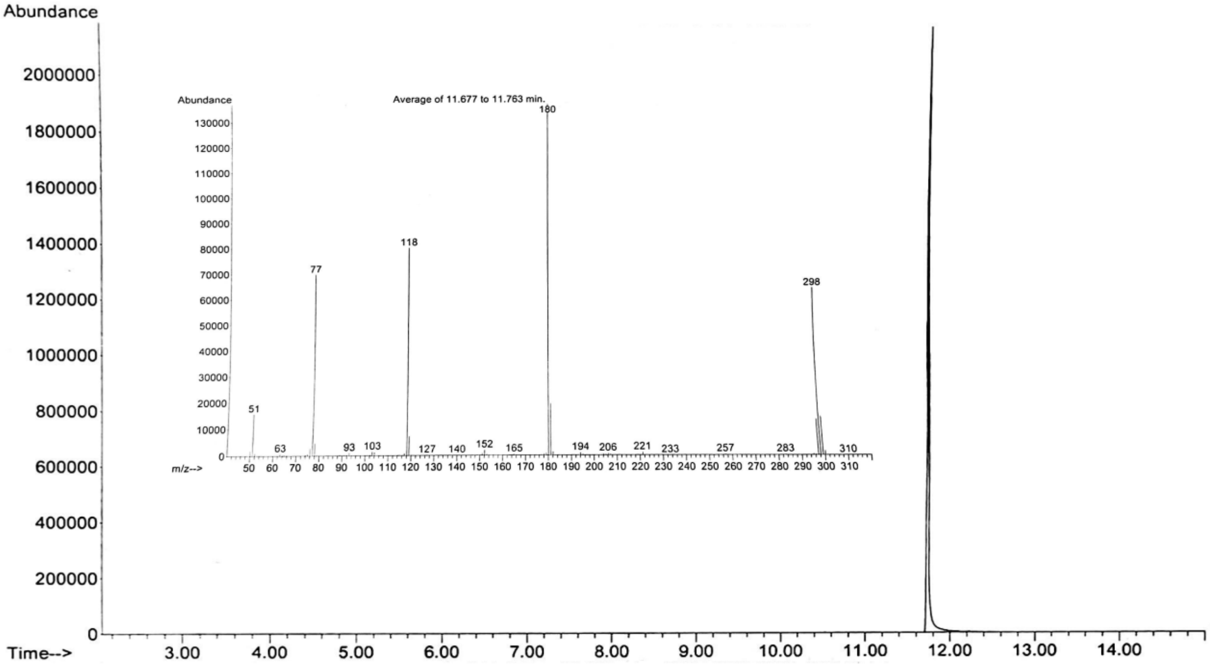
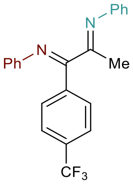


Figure S55. GC-MS of **5f** (m/z = 298).

(4-trifluoromethyl)-*N*^{1},*N*^{2}-diphenylpropane-1,2-diimine (**5g**)



Dark red oil, 102.0 mg. 70% isolated yield. ^{1}H, ^{13}C, and ^{19}F NMR show a mixture of isomers in solution (C_6D_6). GC-MS shows single product peak (m/z = 366), and the diimine was coordinated (**6g**) to $ZnCl_2$ complex to obtain a single isomer and allow for full 1H and 13C assignments (see below).

^{1}H NMR (500 MHz, C_6D_6) (all isomers) δ 8.05 – 7.99 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.15 – 7.10 (m, 7H), 7.10 – 7.05 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.89 (m, 7H), 6.88 – 6.83 (m, 1H), 6.76 (tt, *J* = 7.5, 1.2 Hz, 1H), 6.72 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.71 – 6.66 (m, 3H), 6.66 – 6.61 (m, 4H), 2.25 (s, 3H), 2.06 (s, 1H), 1.36 (s, 3H), 1.18 (s, 1H).
^{13}C NMR (126 MHz, C_6D_6) (all isomers) δ 168.08, 167.13, 166.90, 166.82, 165.77, 164.77, 164.52, 161.00, 152.02, 151.84, 151.19, 150.73, 150.11, 149.89, 149.87, 149.62, 146.76, 143.71, 142.49, 139.58, 138.89, 133.09, 132.98, 132.83, 132.68, 132.58, 132.32, 130.65, 130.31, 130.06, 130.05, 129.44, 129.29, 129.25, 129.13, 129.08, 129.03, 128.99, 128.86, 128.76, 128.25, 128.06, 127.87, 125.89, 125.86, 125.83, 125.79, 125.76, 125.73, 125.70, 125.67, 125.53, 125.45, 125.42, 125.32, 124.81, 124.74, 124.58, 124.55, 124.51, 124.49, 124.36, 121.57, 120.82, 120.74, 120.47, 120.20, 119.47, 118.95, 27.35, 21.86, 20.85, 19.90, 16.02. **^{19}F NMR (471 MHz, C_6D_6)** δ -62.13, -62.69, -62.74, -62.76, -62.81 (vs. TFA) δ -77.80. **ESI-HRMS (m/z):** calcd. for $C_{22}H_{17}F_3N_2Na^+$, 389.1242; found, 389.1242.

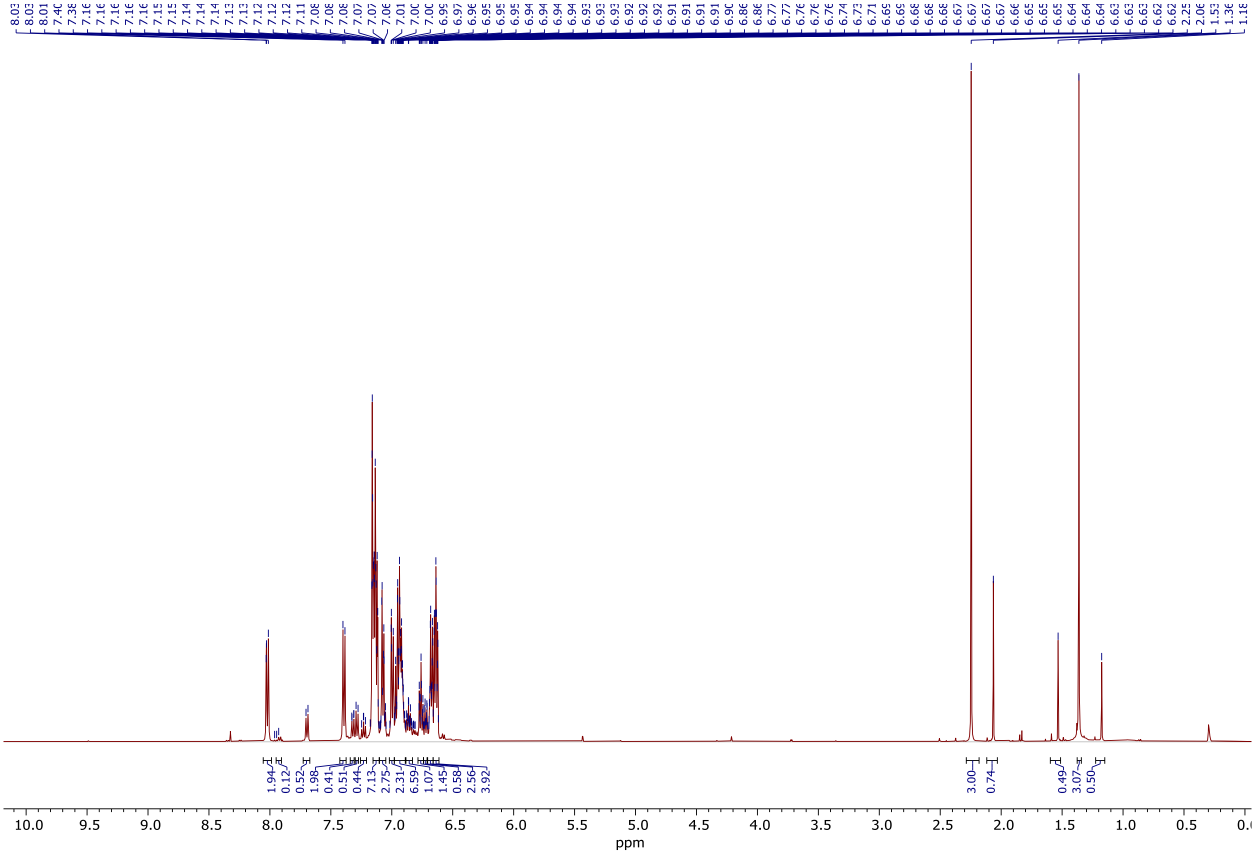


Figure S56. ^{1}H NMR spectrum of **5g** as a mixture of isomers in C_6D_6.

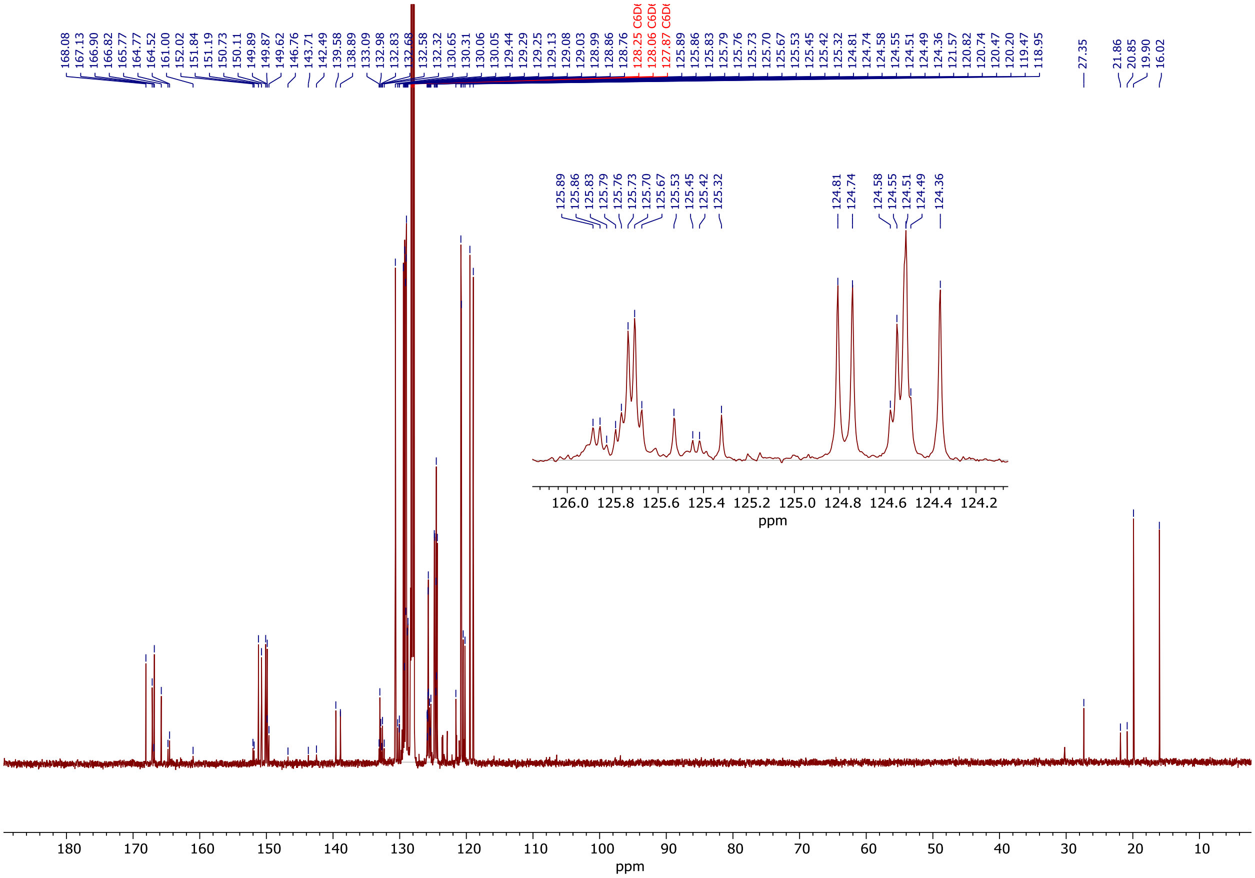


Figure S57. ^{13}C NMR spectrum of **5g** as a mixture of isomers in C_6D_6, with insets showing ortho C quartets.

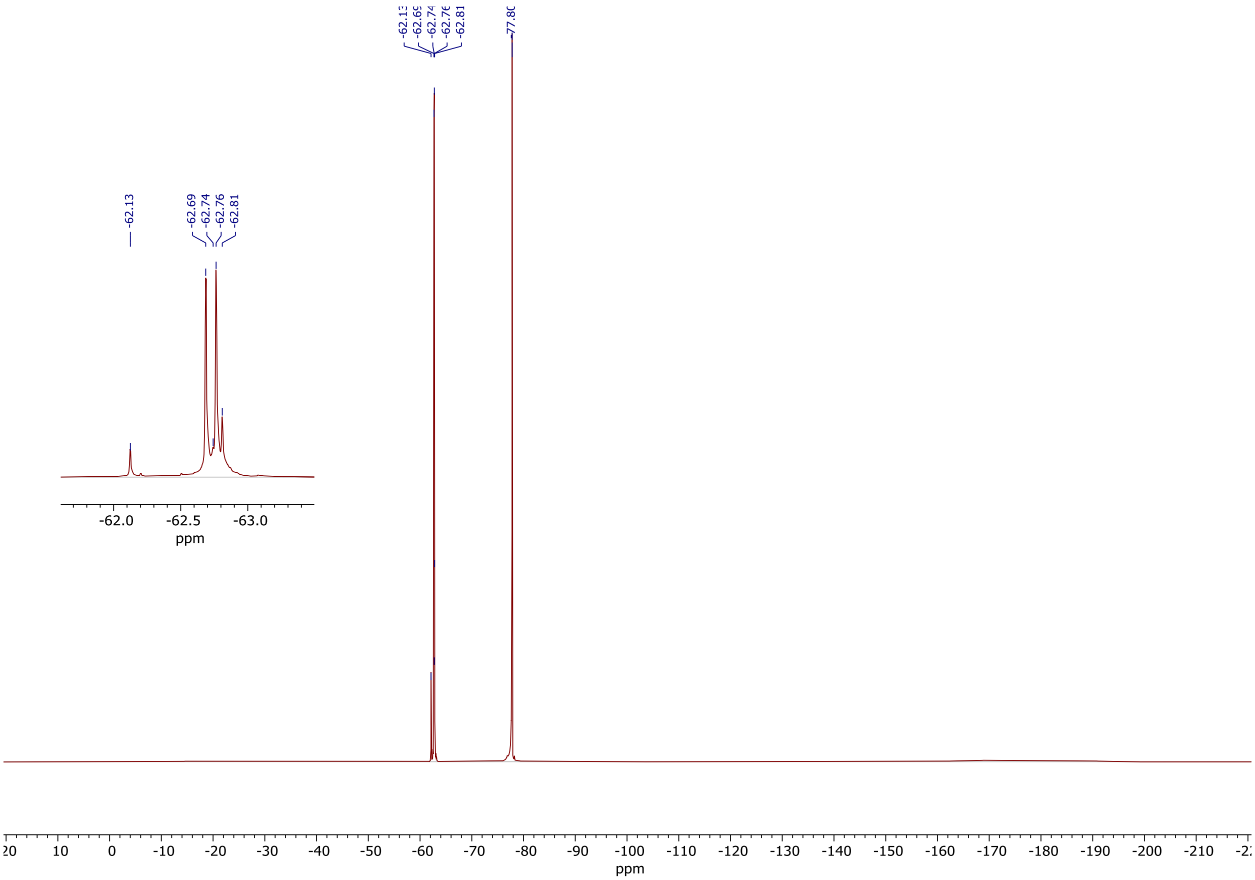


Figure S58. ^{19}F NMR spectrum of **5g** in C_6D_6 with trifluoroacetic acid (neat) reference capillary (δ -77.80), ^{19}F signals for multiple isomers observed.

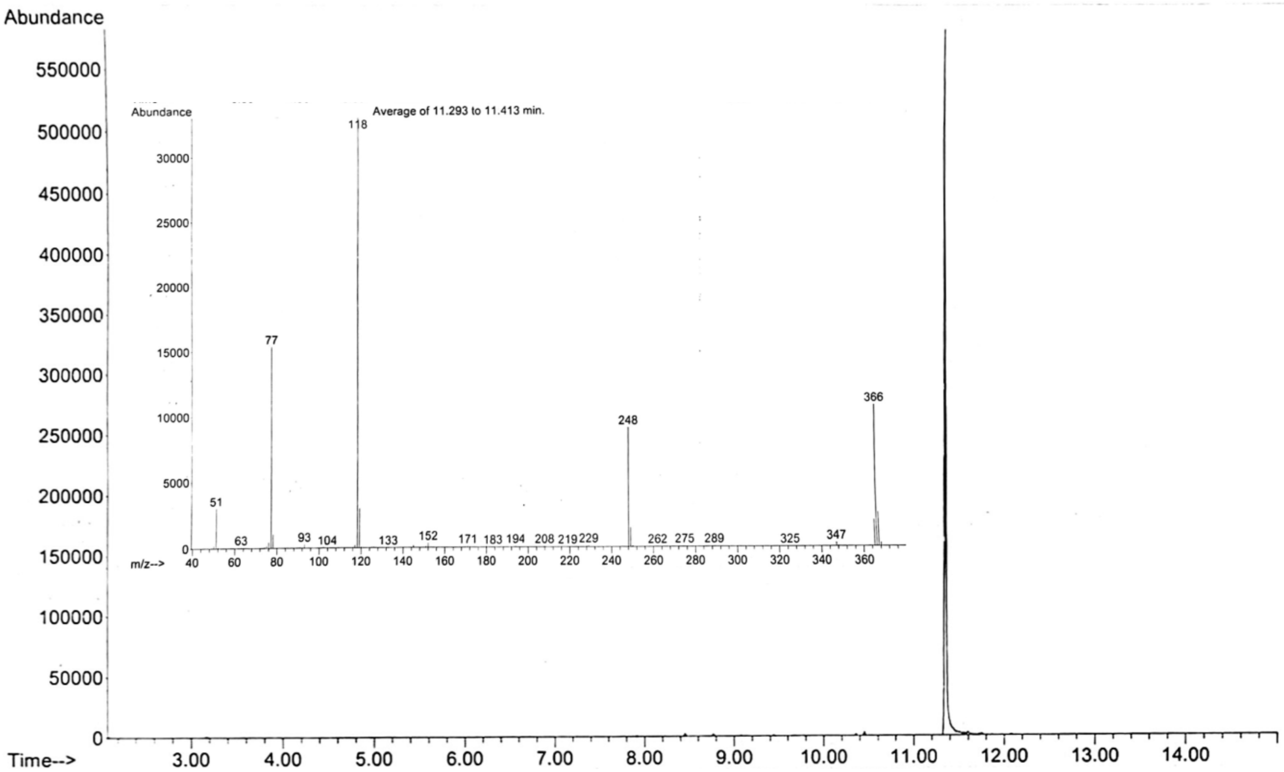
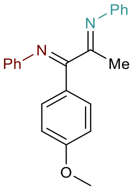


Figure S59. GC-MS of **5g** (m/z = 366).

(4-methoxyphenyl)-N^1,N^2-diphenylpropane-1,2-diimine (**5h**)



Brown oil, 89.1 mg. 68% isolated yield. ^{1}H and ^{13}C NMR show a mixture of isomers in solution (C_6D_6). GC-MS shows single product peak (m/z = 328), and the diimine was coordinated (**6h**) to $ZnCl_2$ complex to obtain a single isomer and allow for full proton and carbon assignments (see below).

^{1}H NMR (500 MHz, C_6D_6) (all isomers) δ 8.25 – 8.15 (m, 2H), 8.02 – 7.98 (m, 1H), 7.92 – 7.84 (m, 1H), 7.28 – 7.18 (m, 1H), 7.15 (d, *J* = 2.0 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.09 – 6.99 (m, 2H), 6.95 – 6.88 (m, 4H), 6.83 – 6.79 (m, 2H), 6.78 – 6.74 (m, 1H), 6.74 – 6.71 (m, 1H), 6.70 – 6.67 (m, 1H), 6.67 – 6.63 (m, 2H), 6.57 – 6.54 (m, 1H), 3.33 (s, 1H), 3.28 (s, 3H), 3.20 (s, 1H), 3.13 (s, 1H), 2.29 (s, 1H), 2.20 (s, 1H), 1.74 (s, 1H), 1.48 (s, 3H), 1.44 (s, 1H). **^{13}C NMR (101 MHz, C_6D_6)** (all isomers) δ 168.76, 168.18, 167.88, 167.55, 165.69, 165.51, 162.66, 162.49, 160.02, 158.65, 153.21, 152.55, 152.09, 151.77, 151.61, 151.29, 150.85, 150.38, 149.97, 134.98, 133.48, 132.24, 131.76, 131.44, 131.38, 131.18, 130.65, 130.36, 130.33, 130.24, 129.38, 129.32, 129.22, 129.20, 129.02, 128.93, 128.90, 128.86, 128.76, 128.30, 128.06, 127.82, 125.09, 124.57, 124.14, 124.01, 123.95, 123.34, 121.72, 121.18, 121.00, 120.94, 120.27, 119.53, 118.93, 114.47, 114.34, 114.15, 113.26, 54.97, 54.91, 54.85, 54.75, 54.57, 28.15, 22.17, 21.01, 20.27, 16.55. **ESI-HRMS (m/z):** calcd. for $C_{22}H_{20}N_2OH^+$, 329.1654; found, 329.1647. (diff. 0.0007)

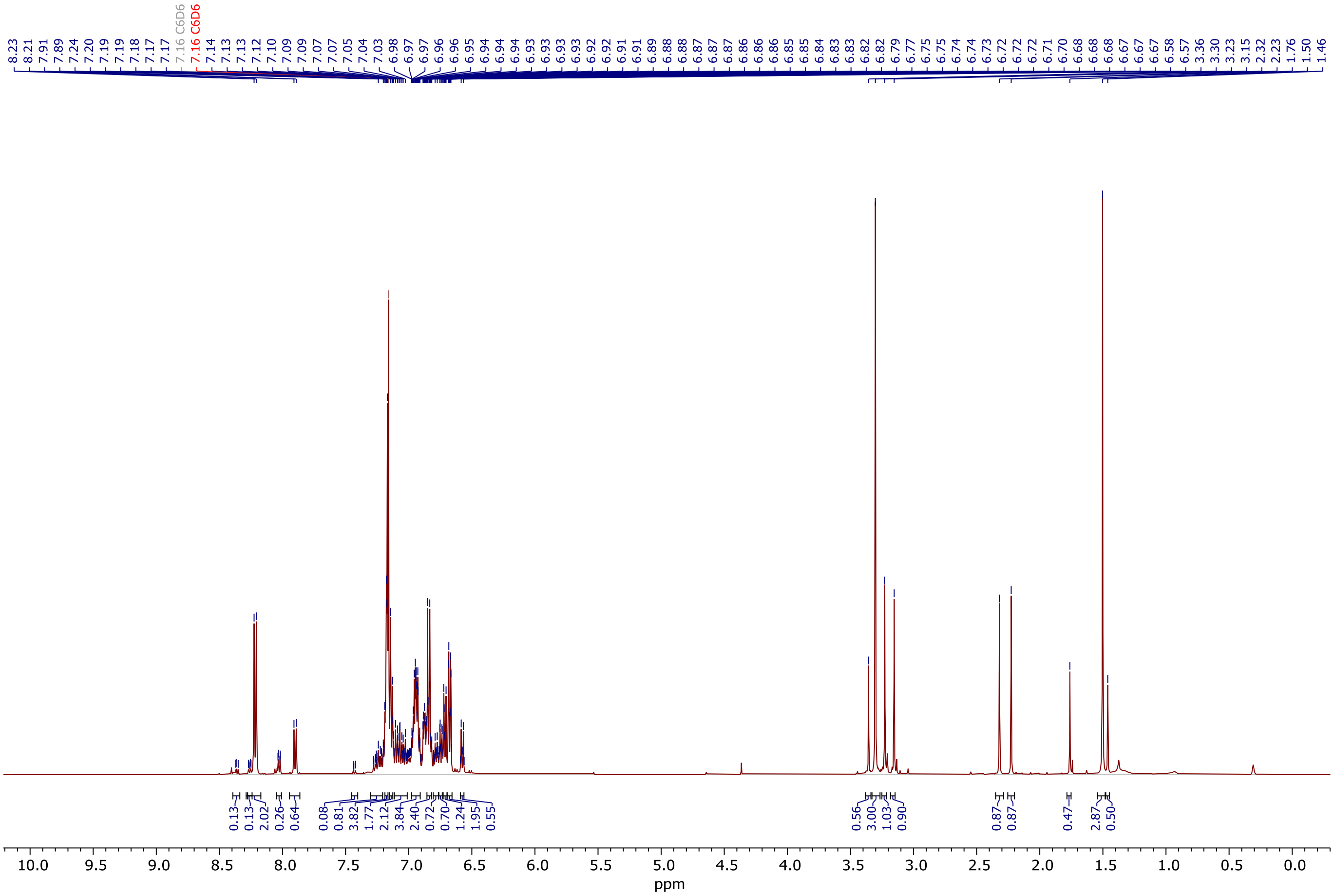


Figure S60. ^{1}H NMR spectrum of **5h** as a mixture of isomers in C_6D_6.

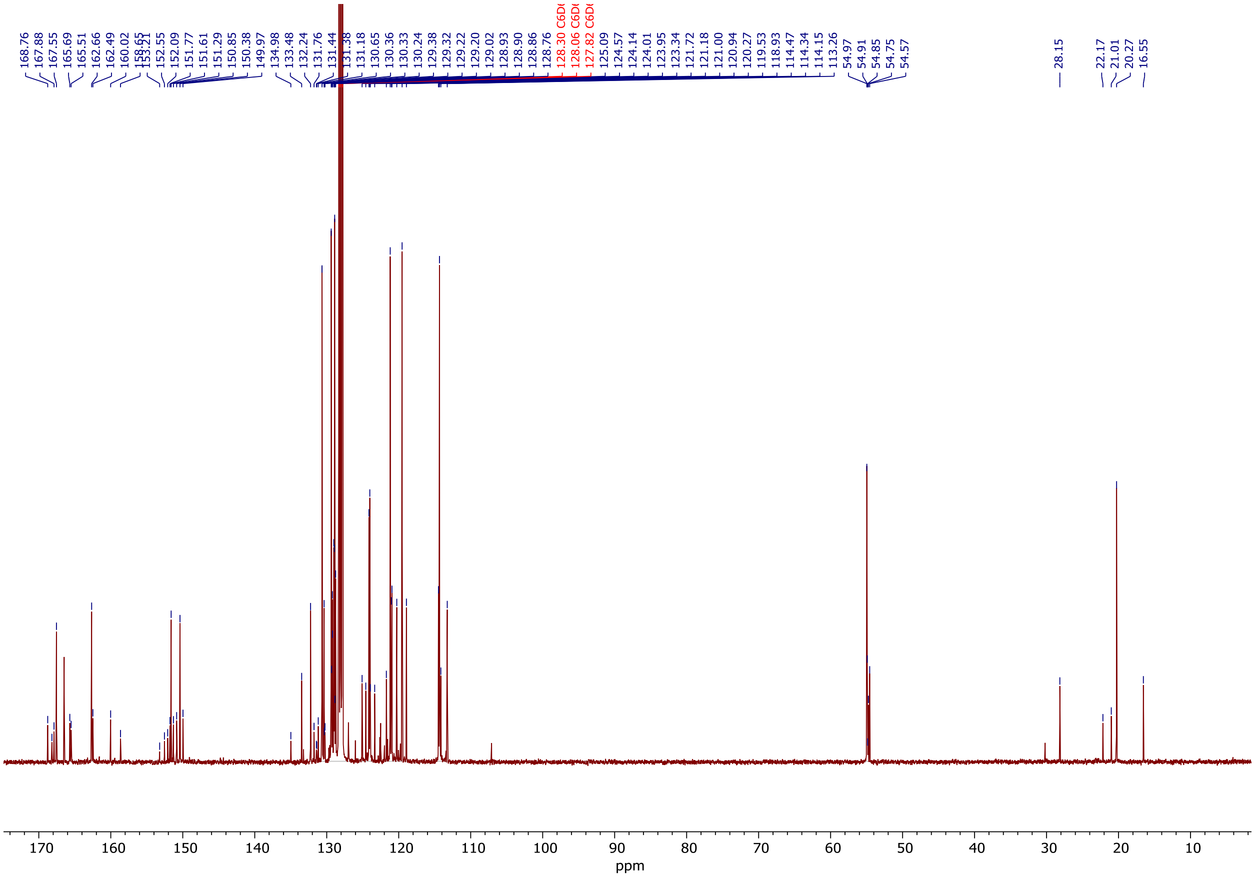


Figure S61. ^{13}C NMR spectrum of **5h** as a mixture of isomers in C_6D_6.

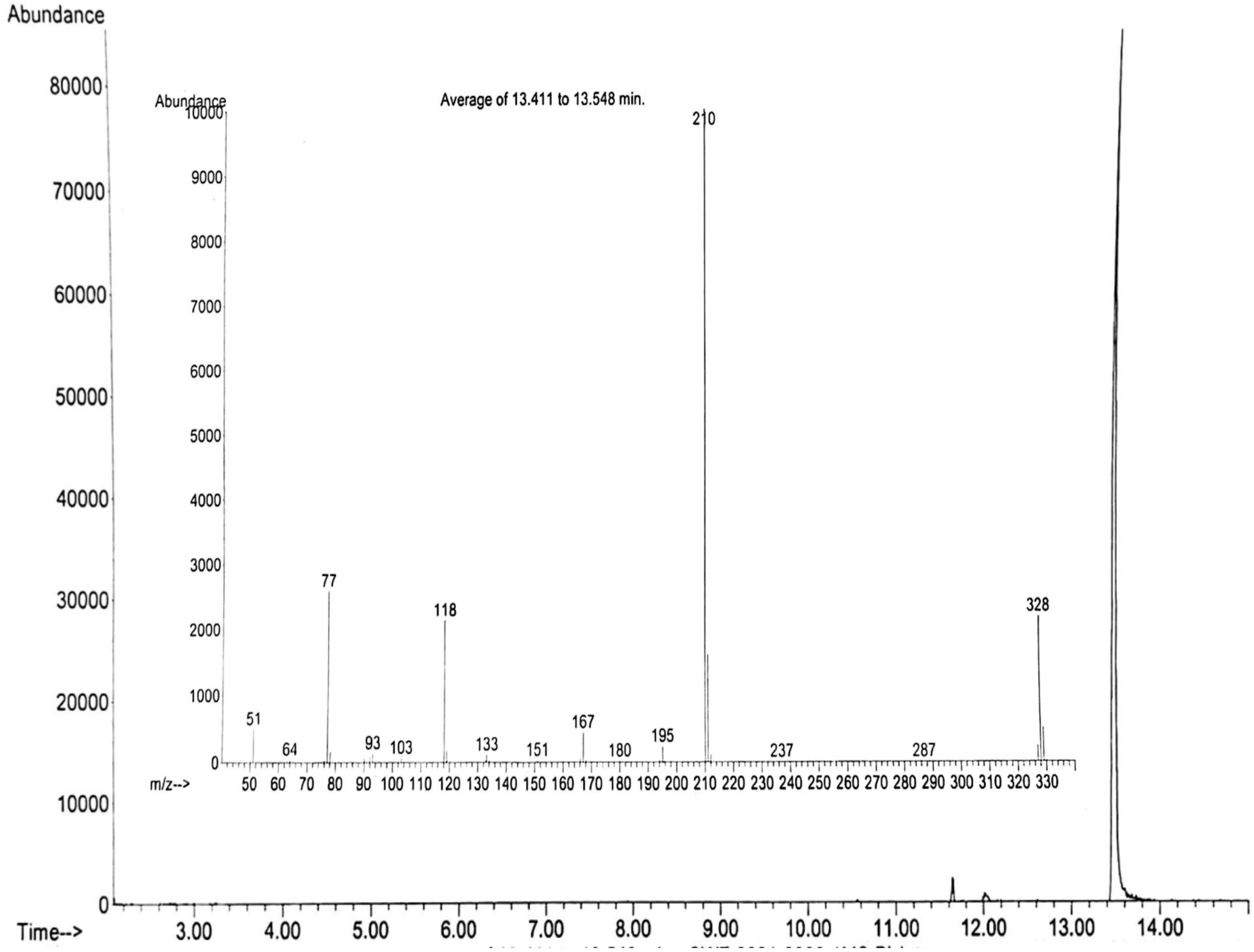
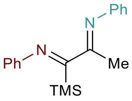


Figure S62. GC-MS of **5h** (m/z =328).

N^1,*N^2*-diphenyl-1-(trimethylsilyl)propane-1,2-diimine (**5i**) **(Not isolated)**



Not isolated, but reaction mixture GC-MS is given. Trace amount of **5i** observed in GC-MS.

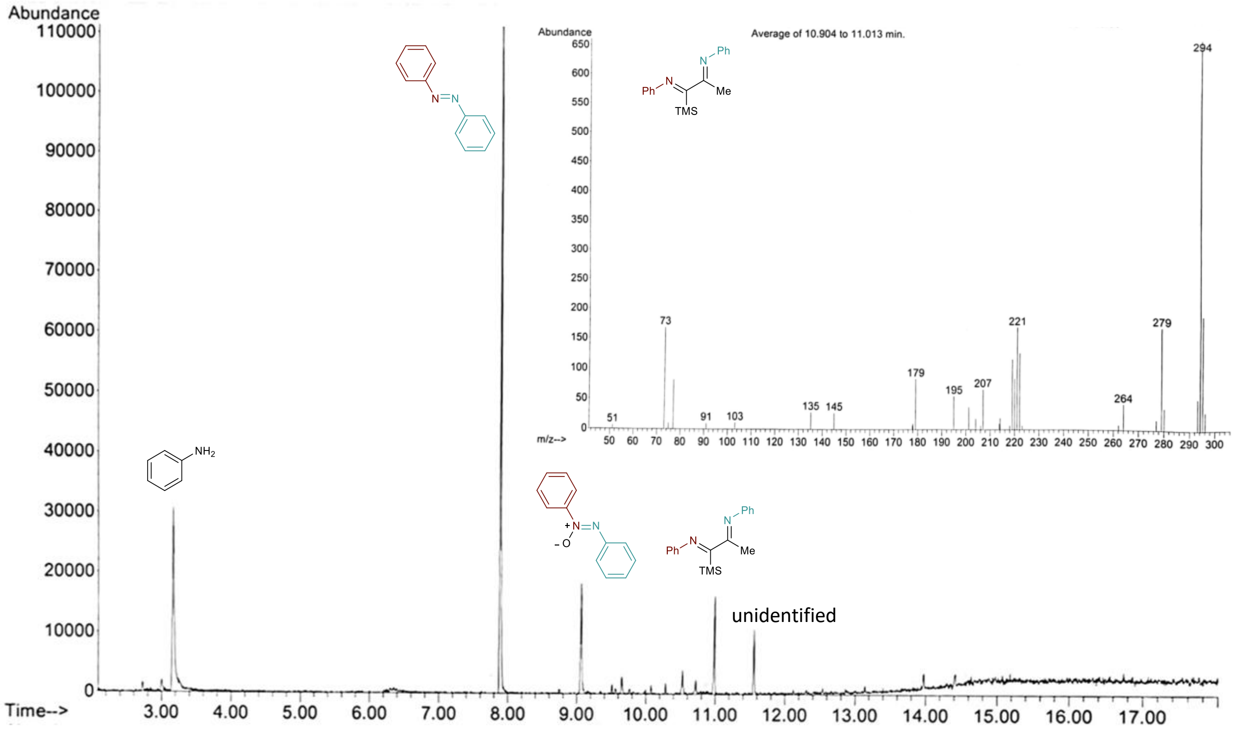
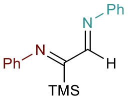


Figure S63. GC-MS of **5i** reaction mixture after workup.

N^1,*N*^{2}-diphenyl-1-(trimethylsilyl)ethane-1,2-diimine (**5j**)



Yellow-brown residue, 31.9 mg. Isolated as a mixture of diimine (26% yield) with some pyrrole impurity (2.4%) (91% pure). ^{1}H and ^{13}C NMR show a mixture of isomers in solution (C_6D_6). Efforts to coordinate to $ZnCl_2$ were unsuccessful. **^{1}H NMR (500 MHz, C_6D_6)** (both isomers) δ 8.31 (s, 1H), 8.12 (s, 1H), 7.14 – 7.07 (m, 7H), 7.07 – 7.02 (m, 4H), 6.98 (m, 6H), 6.95 – 6.86 (m, 10H), 6.79 (m, 5H), 0.57 (s, 9H), 0.17 (s, 6H). **^{13}C NMR (126 MHz, C_6D_6)** δ 185.41, 184.59, 166.27, 155.94, 154.19, 152.50, 150.99, 129.47, 129.42, 129.06, 128.99, 127.49, 127.18, 124.77, 124.53, 121.54, 121.30, 120.24, 118.22, 3.00, 1.53, 0.96, -0.94. **ESI-HRMS (m/z):** calcd. for $C_{17}H_{20}N_2SiNa^+$, 303.1293; found, 303.1271 (diff. 0.0022).

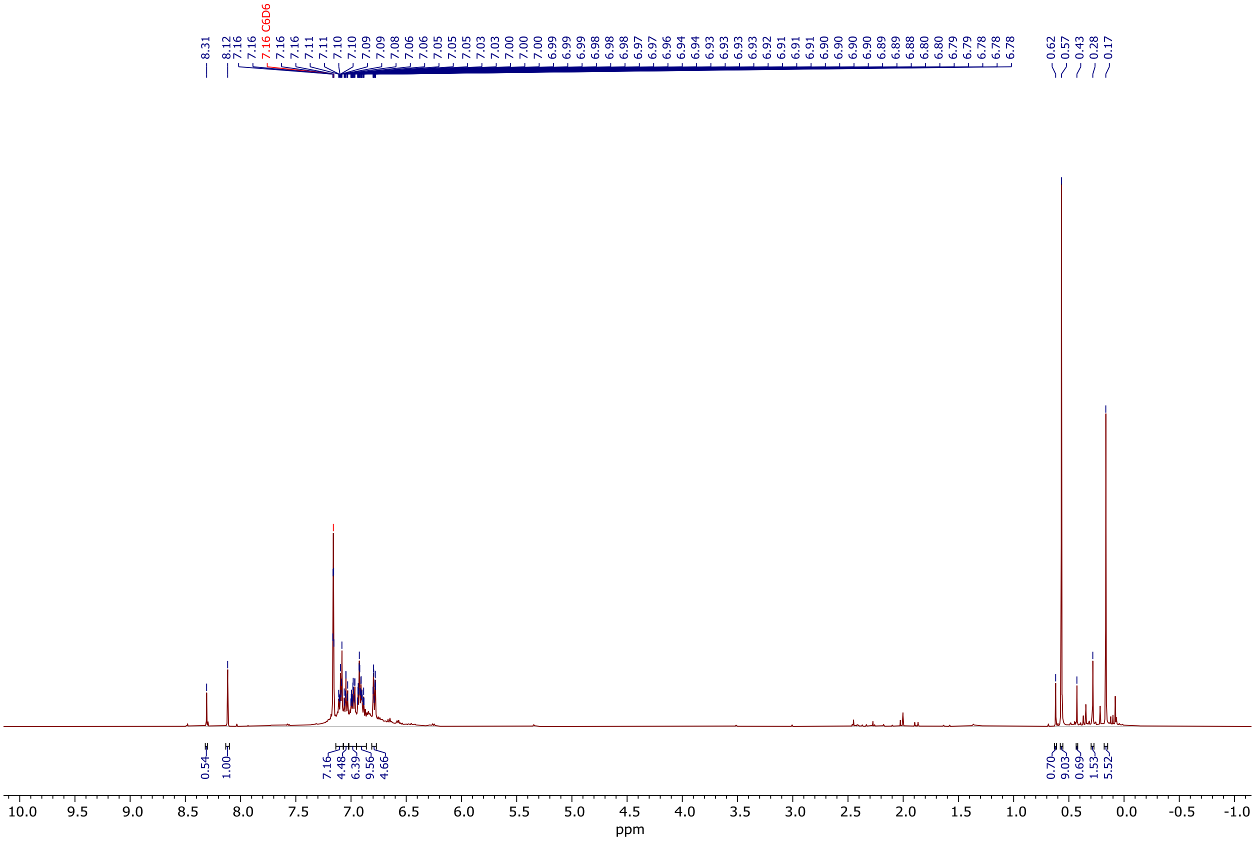


Figure S64. ^{1}H NMR spectrum of **5j** in C_6D_6.

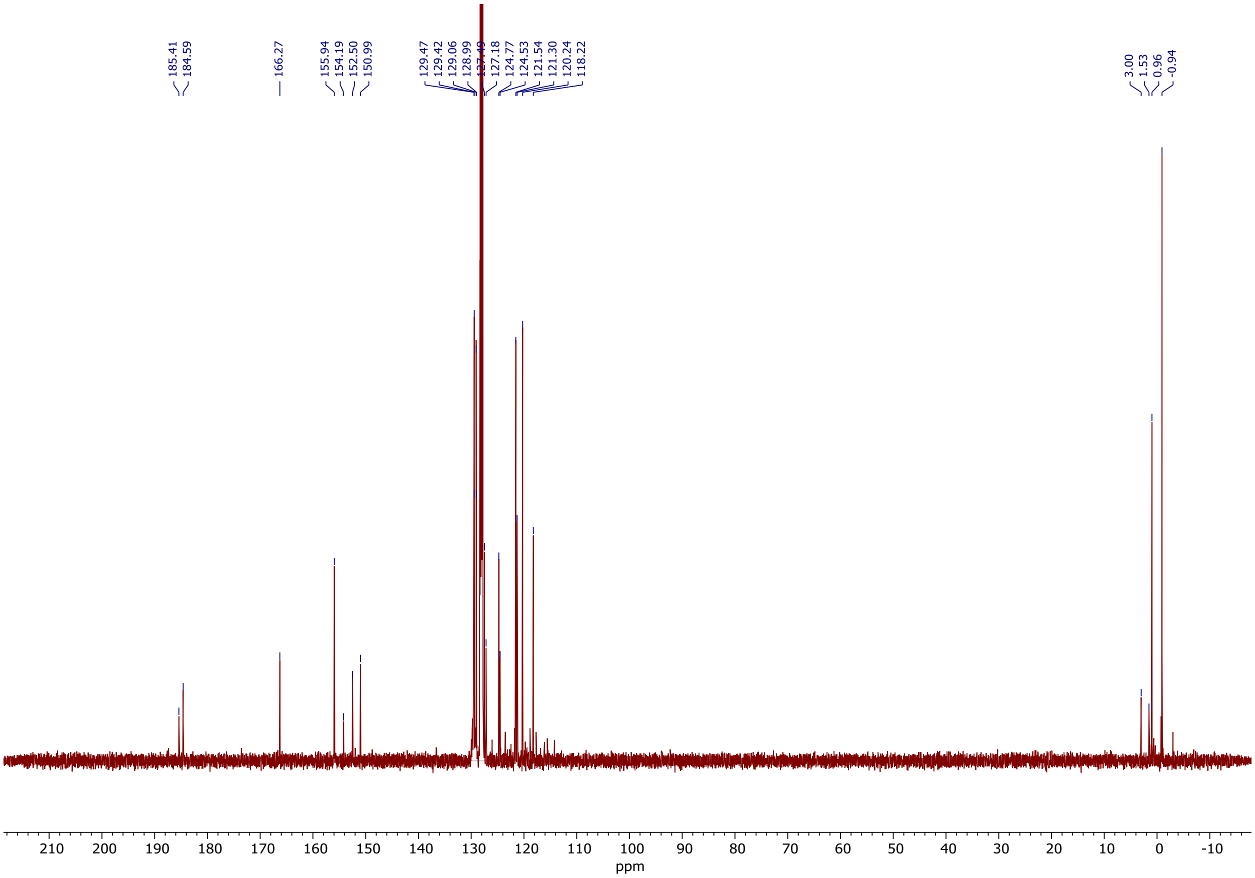
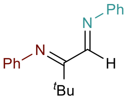


Figure S65. ^{13}C NMR spectrum of **5j** in C_6D_6.

(1E,2E)-3,3-dimethyl-*N*^{1},*N*^{2}-diphenylbutane-1,2-diimine (**5k**)



Yellow oil. 68% isolated yield, 67.2 mg. **^{1}H NMR (400 MHz, C_6D_6)** δ 7.87 (s, 1H, C*H*), 7.04 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.01 – 6.95 (m, 2H, Ar-*H*), 6.94 – 6.90 (m, 1H, Ar-*H*), 6.90 – 6.83 (m, 3H, Ar-*H*), 6.80 – 6.74 (m, 2H, CH(CHC*H*)$_2$CNC(CH$_3$)$_3$), 1.60 (s, 9H, C(C*H$_3$*)$_3$). **^{13}C NMR (101 MHz, C_6D_6)** δ 173.68, 155.60, 151.27, 150.21, 129.41, 129.04, 127.09, 124.28, 123.35, 121.23, 40.66, 28.85. **ESI-HRMS (m/z):** calcd. for $C_{18}H_{20}N_2Na^+$, 265.1705; found, 265.1704. (diff. 0.0001).

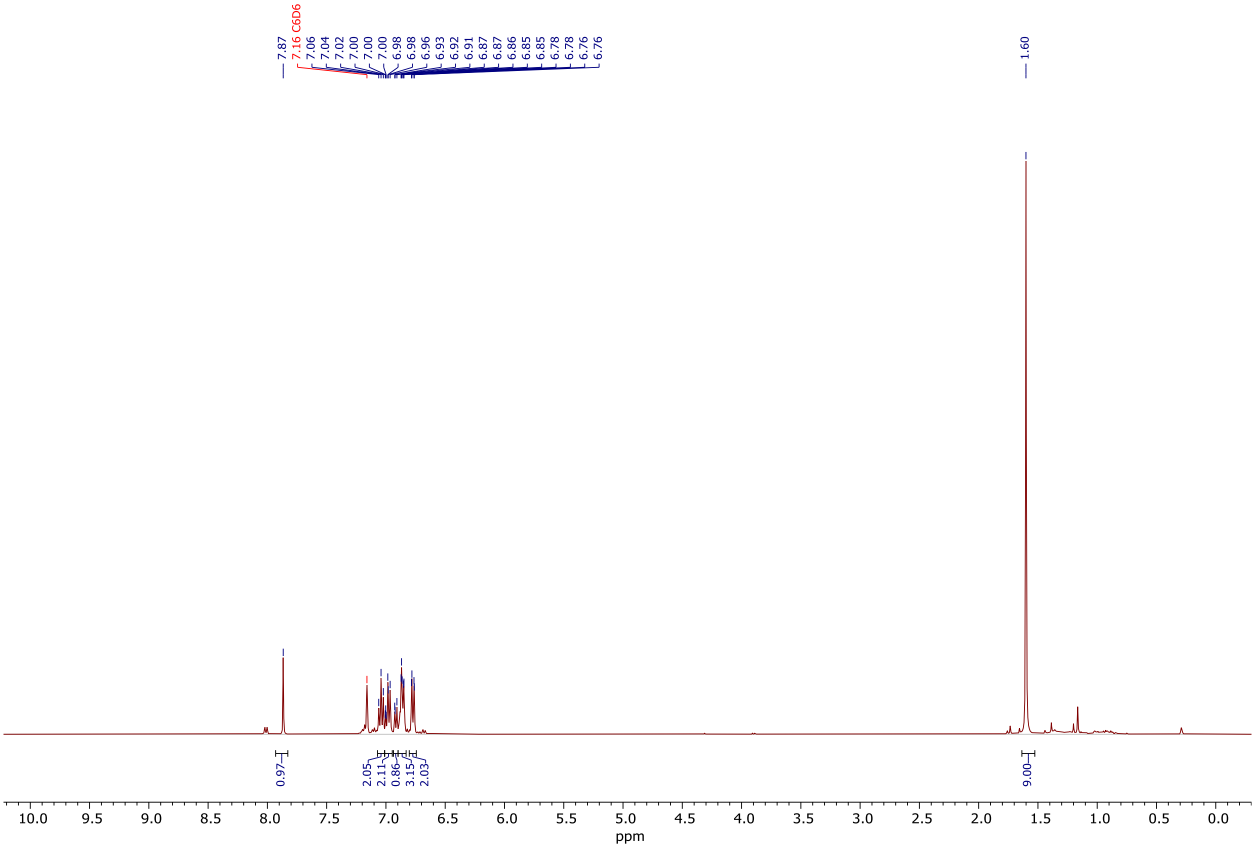


Figure S66. ^{1}H NMR spectrum of **5k** in C_6D_6.

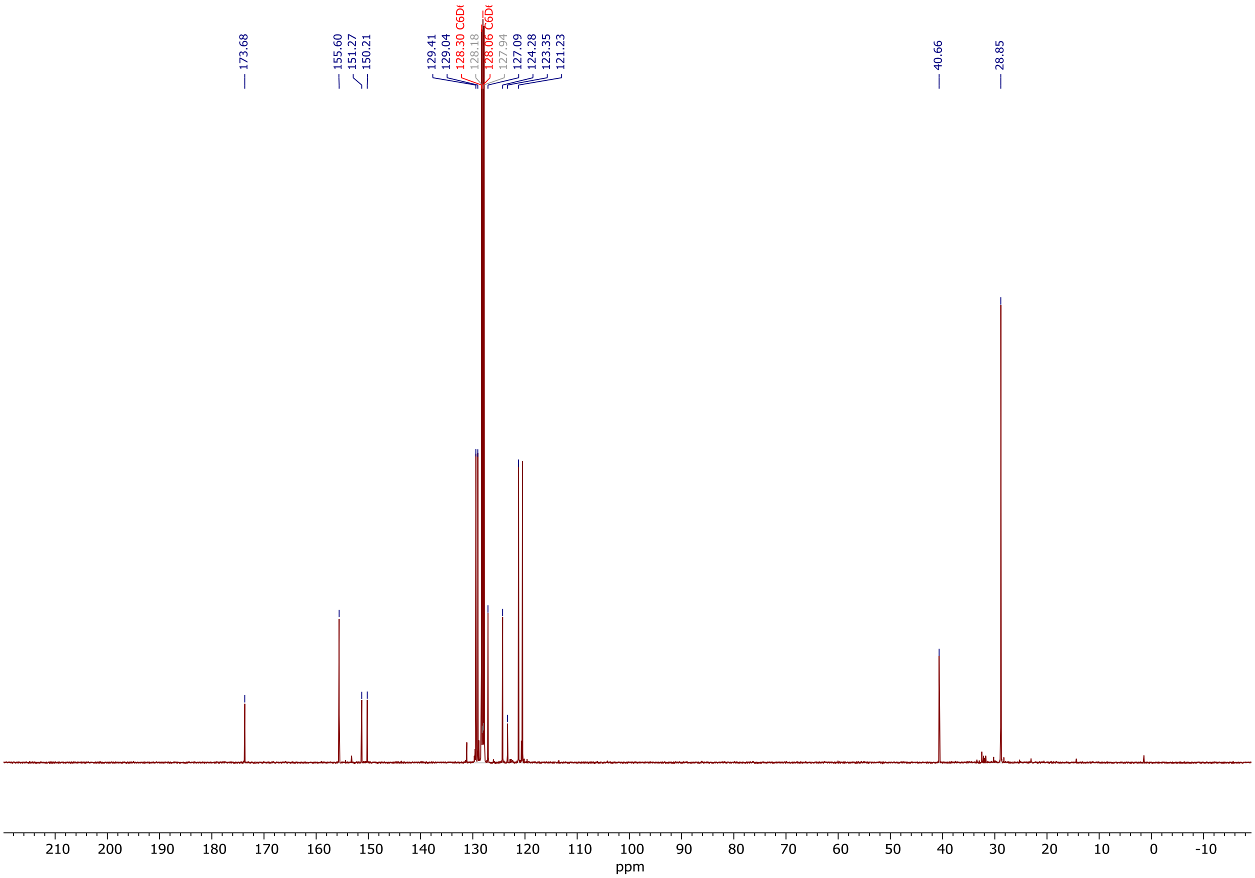
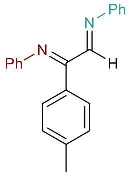


Figure S67. ^{13}C NMR spectrum of **5k** in C_6D_6.

N¹,*N²*-diphenyl-1-(p-tolyl)ethane-1,2-diimine (**5l**)



Brown solid, 94.1 mg. Isolated as a mixture of diimine (66% yield) and pyrrole (12%) (84% pure). ^{1}H and ^{13}C NMR show a mixture of two major isomers in solution (C_6D_6). **ESI-HRMS (m/z):** calcd. for $C_{21}H_{18}N_2H^+$, 299.1548; found, 299.1544 (diff. 0.0004).

^{1}H NMR (500 MHz, C_6D_6) (both isomers) δ 8.59 (s, 1H), 8.31 (d, J = 8.2 Hz, 2H), 8.13 (s, 1H), 7.22 – 7.14 (m, 2H), 7.14 – 6.87 (m, 23H), 6.84 – 6.80 (m, 2H), 2.12 (s, 3H), 1.93 (s, 2H). **^{13}C NMR (126 MHz, C_6D_6)** (both isomers and pyrrole) δ 166.69, 162.87, 162.55, 155.37, 150.84, 150.76, 150.57, 150.03, 140.75, 138.49, 134.41, 131.06, 130.71, 130.48, 130.01, 129.46, 129.35, 129.33, 129.14, 129.09, 128.80, 128.76, 128.63, 128.37, 127.08, 126.99, 125.69, 125.67, 125.24, 124.51, 124.22, 123.74, 122.99, 122.28, 121.14, 121.13, 120.87, 120.83, 21.05, 20.86, 20.74.

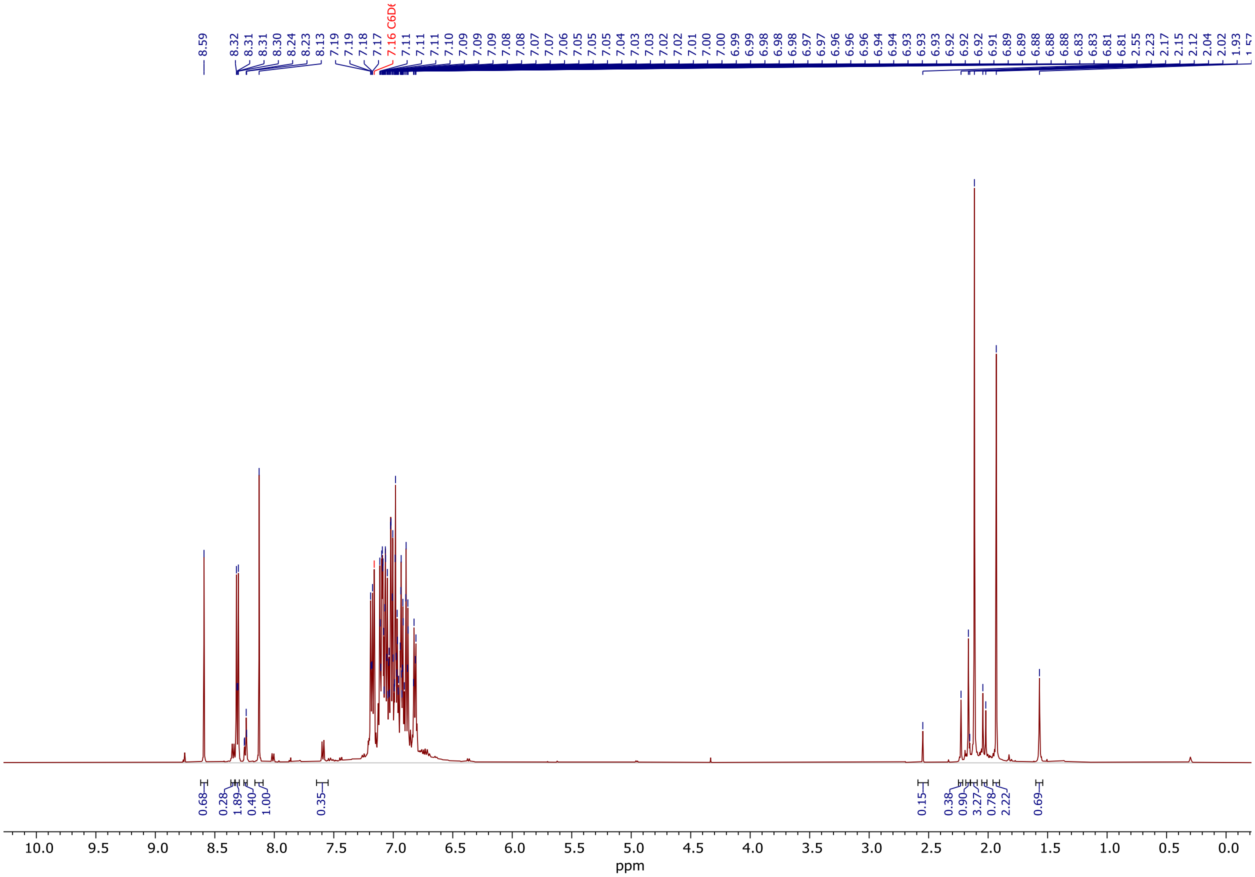


Figure S68. ^{1}H NMR spectrum of **5l** in C_6D_6.

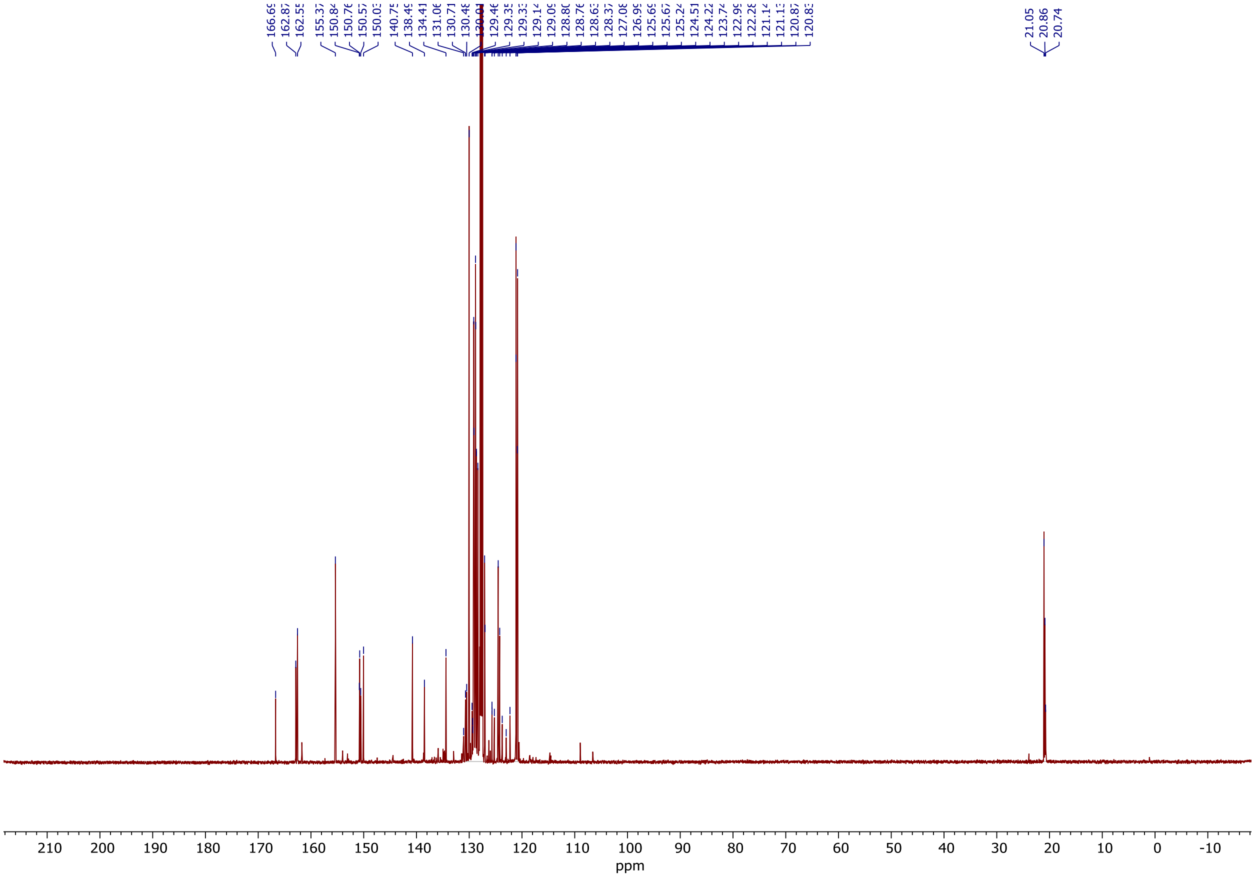
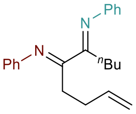


Figure S69. ^{13}C NMR spectrum of **5l** in C_6D_6.

(5E,6E)-N^5,N^6-diphenyldec-1-ene-5,6-diimine (**5m**)



Reddish-brown oil, 64.3 mg. 50% isolated yield. **^{1}H NMR (500 MHz, C$_6$D$_6$)** δ 7.22 – 7.17 (m, 2H), 7.16 – 7.14 (m, 2H), 6.97 – 6.90 (m, 2H), 6.82 – 6.70 (m, 4H), 5.64 (ddt, *J* = 16.9, 10.1, 6.8 Hz, 1H, CH$_2$CH$_2$C*H*=CH$_2$), 4.94 (dd, *J* = 17.0, 1.7 Hz, 1H, CH$_2$CH$_2$CH=C*H$_2$*), 4.86 (dd, *J* = 10.1, 1.7 Hz, 1H, CH$_2$CH$_2$CH=C*H$_2$*), 2.92 – 2.83 (m, 2H, C*H$_2$*CH$_2$CH=CH$_2$), 2.83 – 2.71 (m, 2H, C*H$_2$*CH$_2$CH$_2$CH$_3$), 2.35 (q, *J* = 7.5 Hz, 2H, CH$_2$C*H$_2$*CH=CH$_2$), 1.58 (p, *J* = 7.8 Hz, 2H, CH$_2$C*H$_2$*CH$_2$CH$_3$), 1.16 (h, *J* = 7.4 Hz, 2H, CH$_2$CH$_2$C*H$_2$*CH$_3$), 0.73 (t, *J* = 7.4 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H$_3$*). **^{13}C NMR (101 MHz, C$_6$D$_6$)** δ 170.99, 170.14, 151.46, 151.34, 137.80, 129.27, 129.25, 123.81, 123.77, 118.81, 118.78, 115.23, 32.67, 30.67, 28.41, 28.11, 23.22, 13.90. **ESI-HRMS (m/z):** calcd. for $C_{22}H_{26}N_2Na^+$, 341.1994; found, 341.1999. (diff. 0.0005).

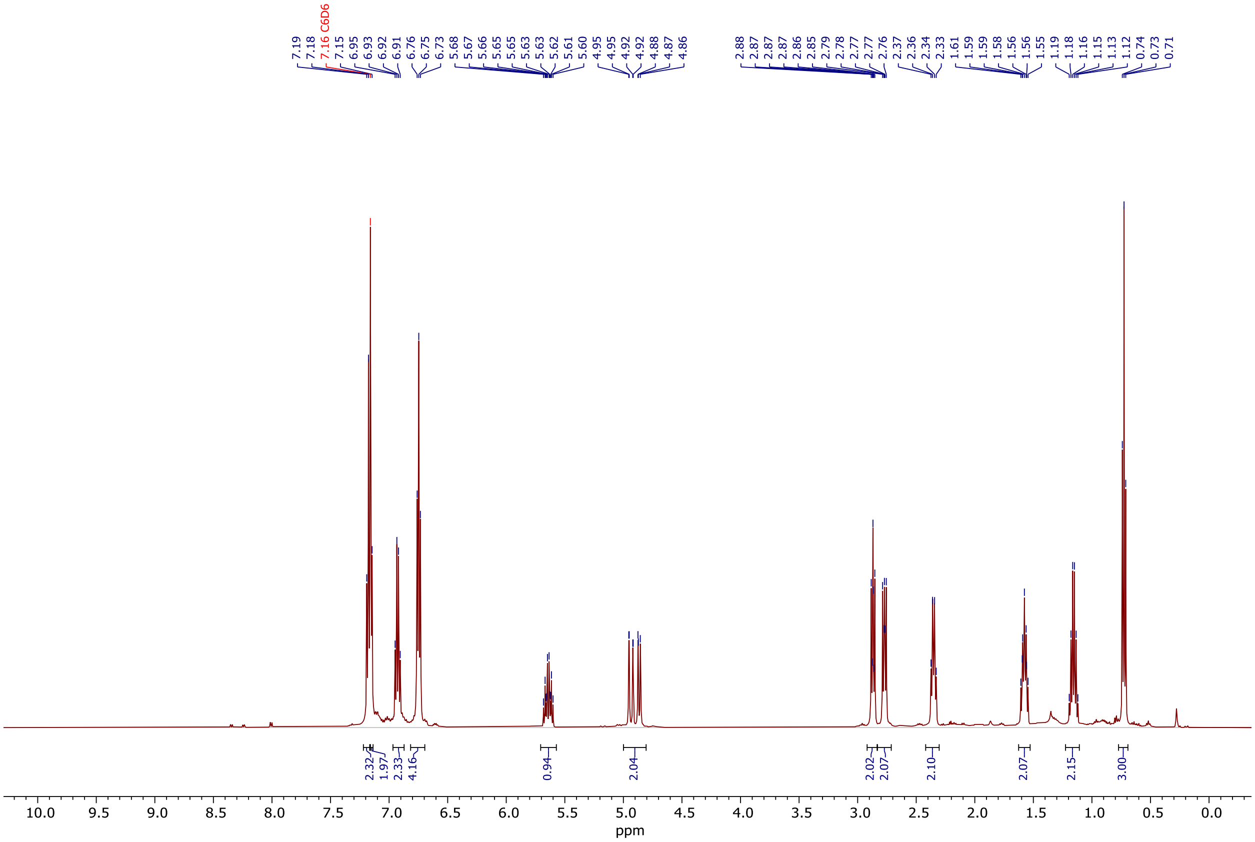


Figure S70. ^{1}H NMR spectrum of **5m** in C$_6$D$_6$.

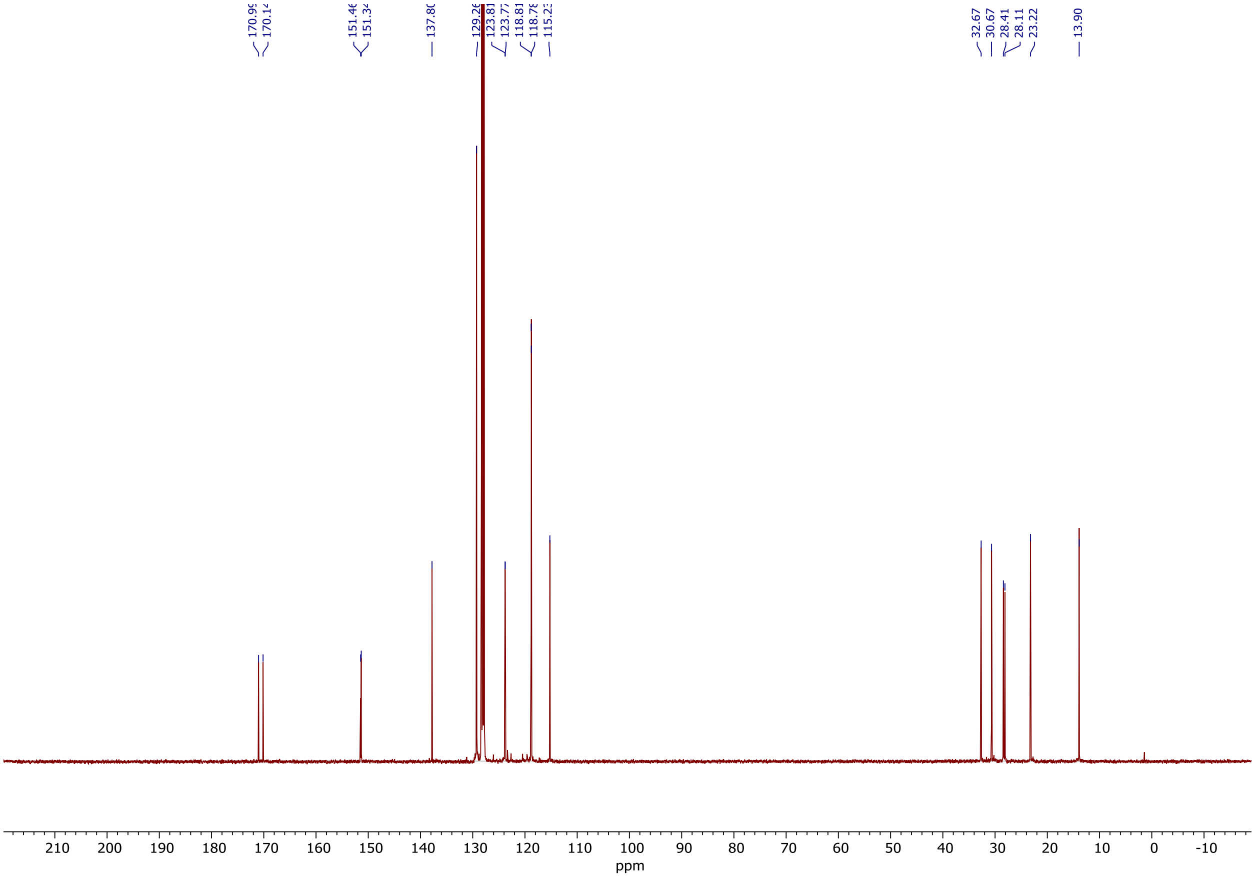
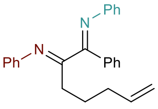


Figure S71. ^{13}C NMR spectrum of **5m** in C_6D_6.

(1E,2E)-N^1,*N*^{2}-1-triphenylhept-6-ene-1,2-diimine (**5n**) (Not isolated)



Not isolated, 10% yield of diimine, with 6% combined yield of two carboamination products as determined by GC-FID (Figure S71) using 1,3,5-trimethoxybenzene as an internal standard (45.8 mg). Product identities determined by GC-MS (Figure S70).

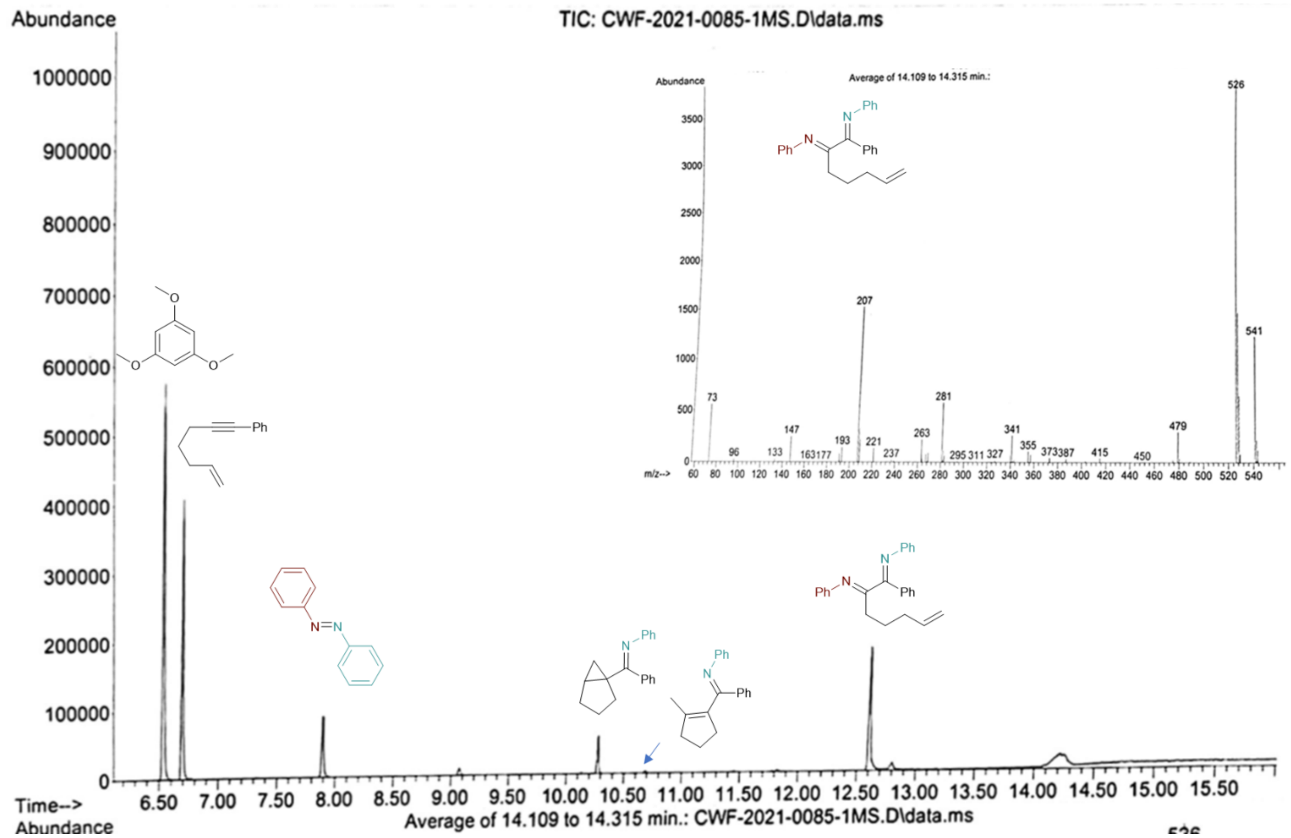


Figure S72. GC-MS of **5n** reaction mixture in C_6D_6.

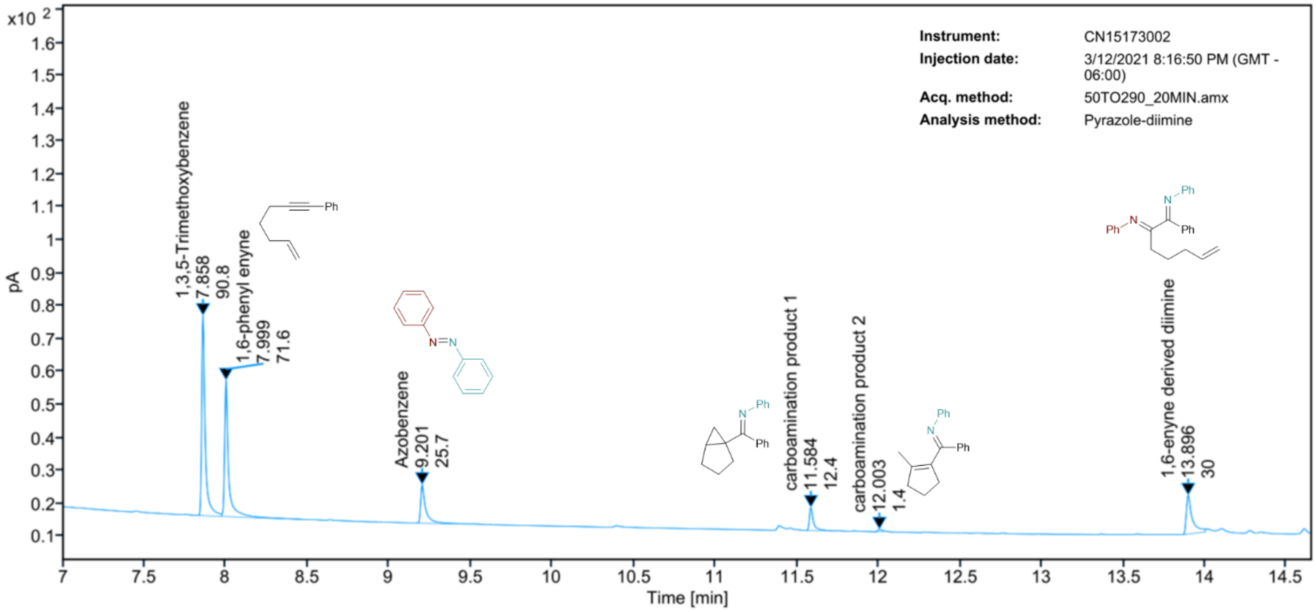
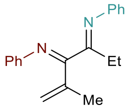


Figure S73. GC-FID of **5n** reaction mixture.

(3E,4E)-2-methyl-N^3,N^4-diphenylhex-1-ene-3,4-diimine (**5o**) (Not isolated)



Not isolated, but reaction mixture GC-MS is given. Trace amount of **5o** observed in GC-MS, alongside some hydrolyzed **5o**.

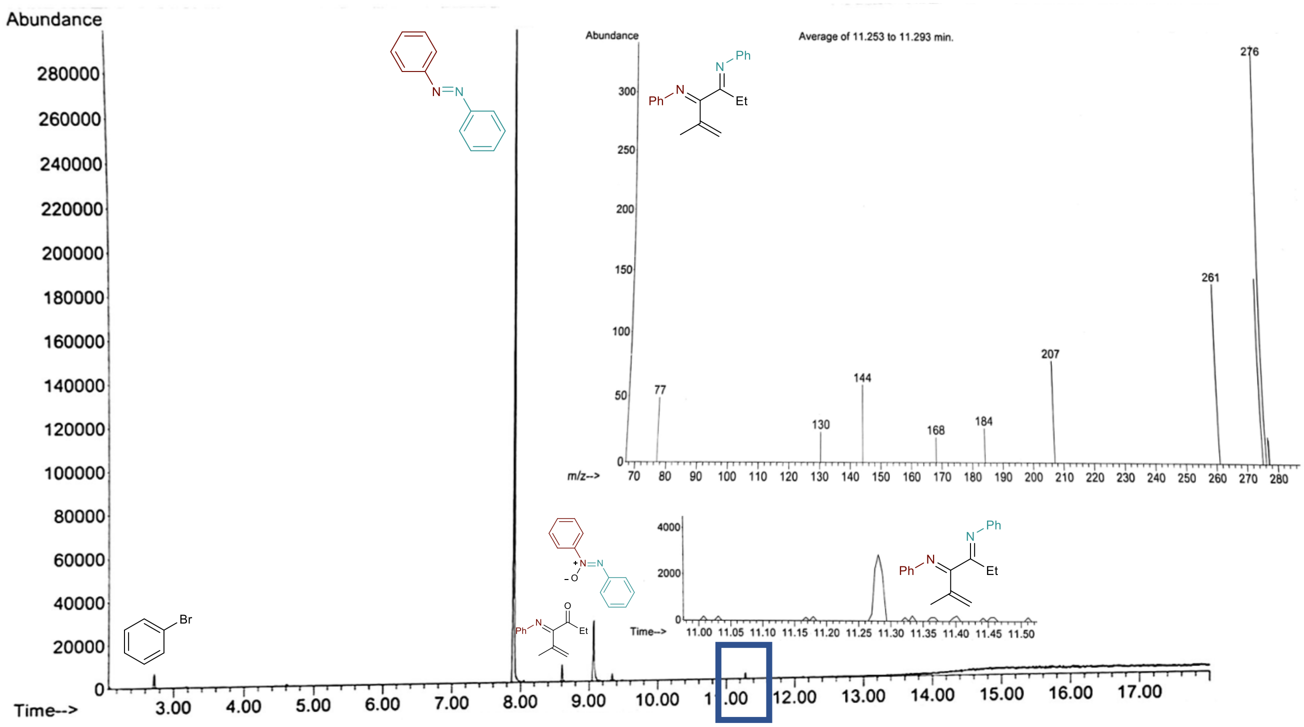
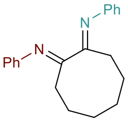


Figure S74. ^{13}C NMR spectrum of **5n** in C_6D_6.

(1E,2E)-N^1,*N*^{2}-diphenylcyclooctane-1,2-diimine (**5p**) (Not isolated or detected)



Not isolated, but reaction mixture NMR and GC-MS is given. Trimer was the major reaction product, with a small amount of pyrrole. A trace amount of **5p** was observed in the baseline of the GC-MS.

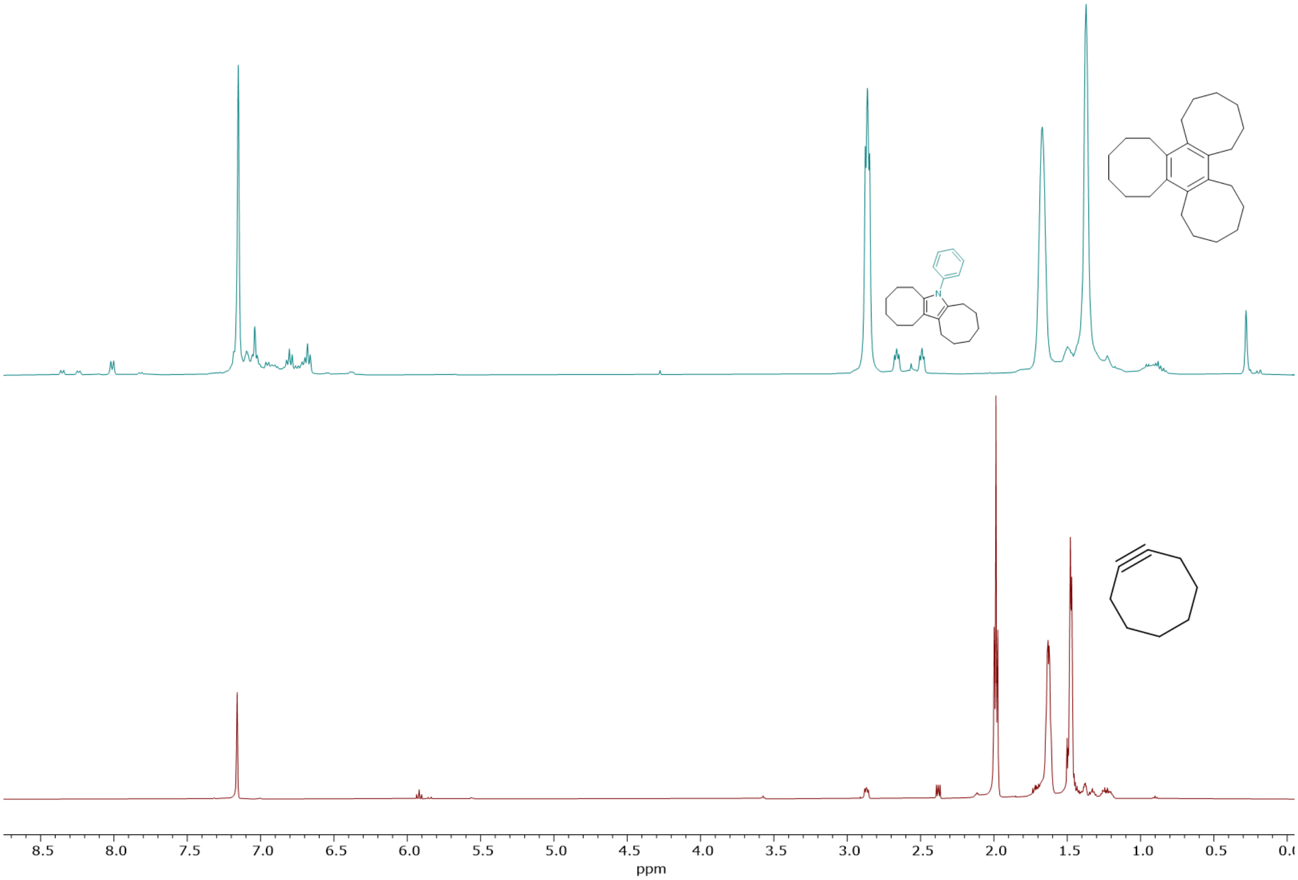


Figure S75. ^{1}H NMR spectrum of **5p** reaction mixture after workup (top) and cyclooctyne **4p** (bottom) in C_6D_6.

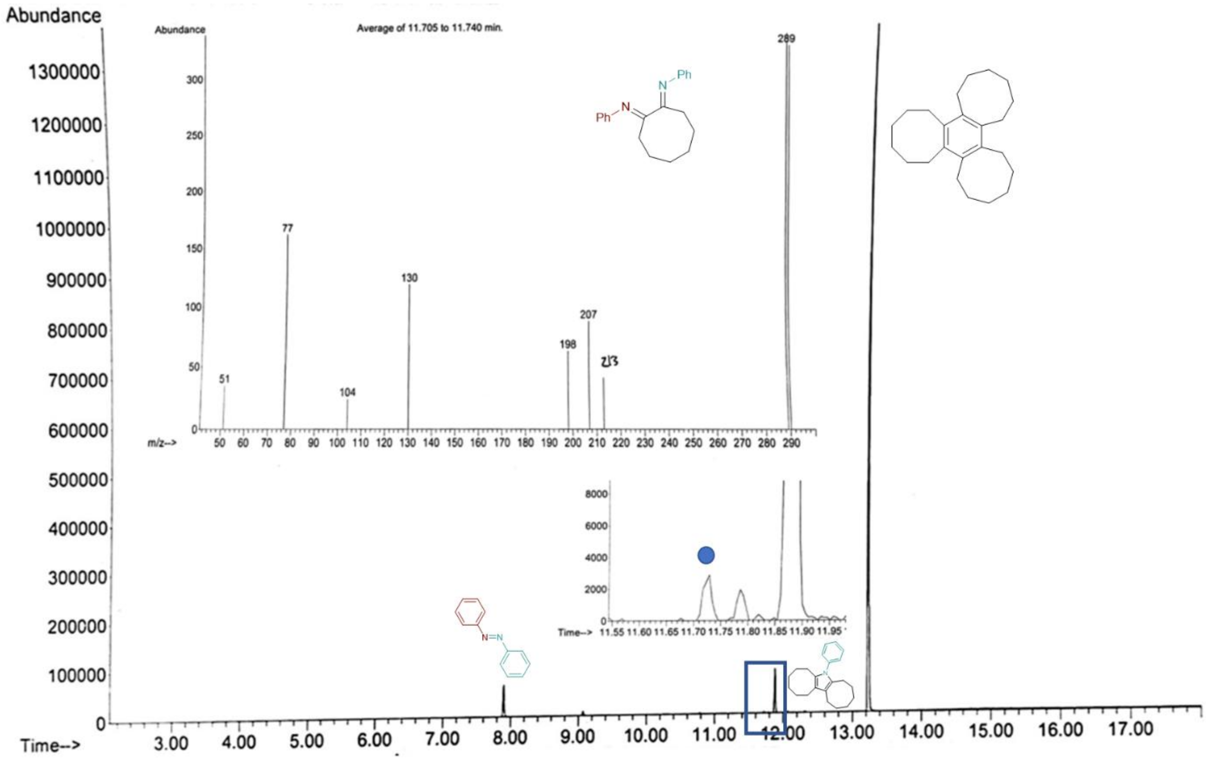
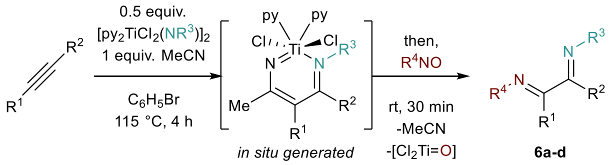


Figure S76. GC-MS of **5p** reaction mixture after workup (m/z = 290).

Modular synthesis of diimine regioisomers (**5q-5r**)

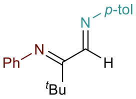


For **5q**: $[\text{py}_2\text{TiCl}_2(\text{N}p\text{-tol})]_2$ (152.8 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 µL, 4.00 mmol, 10 equiv.), and *tert*-butylacetylene (0.400 mmol, 1.00 equiv, 50 µL). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 ˚C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene (**2a**) (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na_2CO_3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na_2SO_4, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and any remaining *tert*-butylacetylene) were reduced under vacuum. Any remaining diazene (from the metathesis of leftover imido with nitrosobenzene) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum. 45.8 mg of an orange solid (41% yield) was isolated and a ^{1}H NMR spectrum was recorded.

For **5r**: $[\text{py}_2\text{TiCl}_2(\text{NPh})]_2$ (147.2 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 µL, 4.00 mmol, 10 equiv.), and *tert*-butylacetylene (0.400 mmol, 1.00 equiv, 50 µL). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 ˚C for 4 h while stirring. The heterogeneous yellow-orange mixture turned dark brown-yellow upon heating. After the initial heating period, the vial was brought back into the glovebox, and p-tolNO (**2g**) (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na_2CO_3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na_2SO_4, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and any remaining *tert*-butylacetylene) were reduced under vacuum. Any remaining diazene (from the metathesis of leftover imido with **2g**) was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum. 49.4 mg of an orange oil (44% yield) was isolated and a ^{1}H NMR spectrum was recorded.

For **5s**: $[\text{py}_2\text{TiCl}_2(\text{N}^t\text{Bu})]_2$ (139.2 mg, 0.400 mmol, 1 equiv.), PhBr (4 mL), and a stir bar were added to a 20 mL scintillation vial, followed by acetonitrile (208 µL, 4.00 mmol, 10 equiv.), and *p*-toluacetylene (0.400 mmol, 1.00 equiv, 51 µL). The vial was sealed with a Teflon cap, wrapped in electrical tape, brought out of the glovebox, and placed in a preheated oil bath at 115 ˚C for 4 h while stirring. The heterogeneous orange-pink mixture turned dark brown upon heating. After the initial heating period, the vial was brought back into the glovebox, and nitrosobenzene (**2a**) (42.8 mg, 0.4 mmol, 1 equiv.) was added with an additional 0.5 mL PhBr. The mixture was allowed to stir for 30 minutes. The vial was then removed from the glovebox and was quenched by the addition of 10 mL of saturated Na_2CO_3 (aq). The layers were separated, and the aqueous layer was extracted with DCM. The organics were combined, dried over Na_2SO_4, and filtered. The volatiles (including bromobenzene, DCM, MeCN, and any remaining *p*-toluacetylene) were reduced under vacuum. Any remaining diazene was then removed through sublimation using a water-cooled cold finger with a ground glass joint fitted into to a round bottom flask, which was heated at 70 °C under vacuum. 60.2 mg of an orange oil (50% yield of diimine, 4% yield of pyrrole) was isolated and a ^{1}H NMR spectrum was recorded.

(1E,2E)-3,3-dimethyl-*N*^{2}-phenyl-*N*^{1}-(p-tolyl)butane-1,2-diimine (**5q**)



Orange solid, 45.8 mg. 41% isolated yield. **^{1}H NMR (400 MHz, C_6D_6)** δ 7.95 (s, 1H, C*H*), 7.08 – 7.02 (m, 2H, CH(C*H*CH)$_2$CN), 6.91 – 6.83 (m, 3H, CH_3C(C*H*CH)$_2$CN & C*H*(CHCH)$_2$CN), 6.82 – 6.76 (m, 4H, CH(CHC*H*)$_2$CN & CH_3C(CHC*H*)$_2$CN), 2.00 (s, 3H, C*H*$_3$), 1.63 (s, 9H, C(C*H*$_3$)$_3$). **^{13}C NMR (101 MHz, C_6D_6)** δ 173.76, 154.48, 150.37, 148.76, 137.04, 130.07, 129.04, 124.18, 121.34, 120.46, 40.68, 28.91, 20.90. **ESI-HRMS (m/z):** calcd. for $C_{19}H_{22}N_2Na^+$, 301.1681; found, 301.1681.

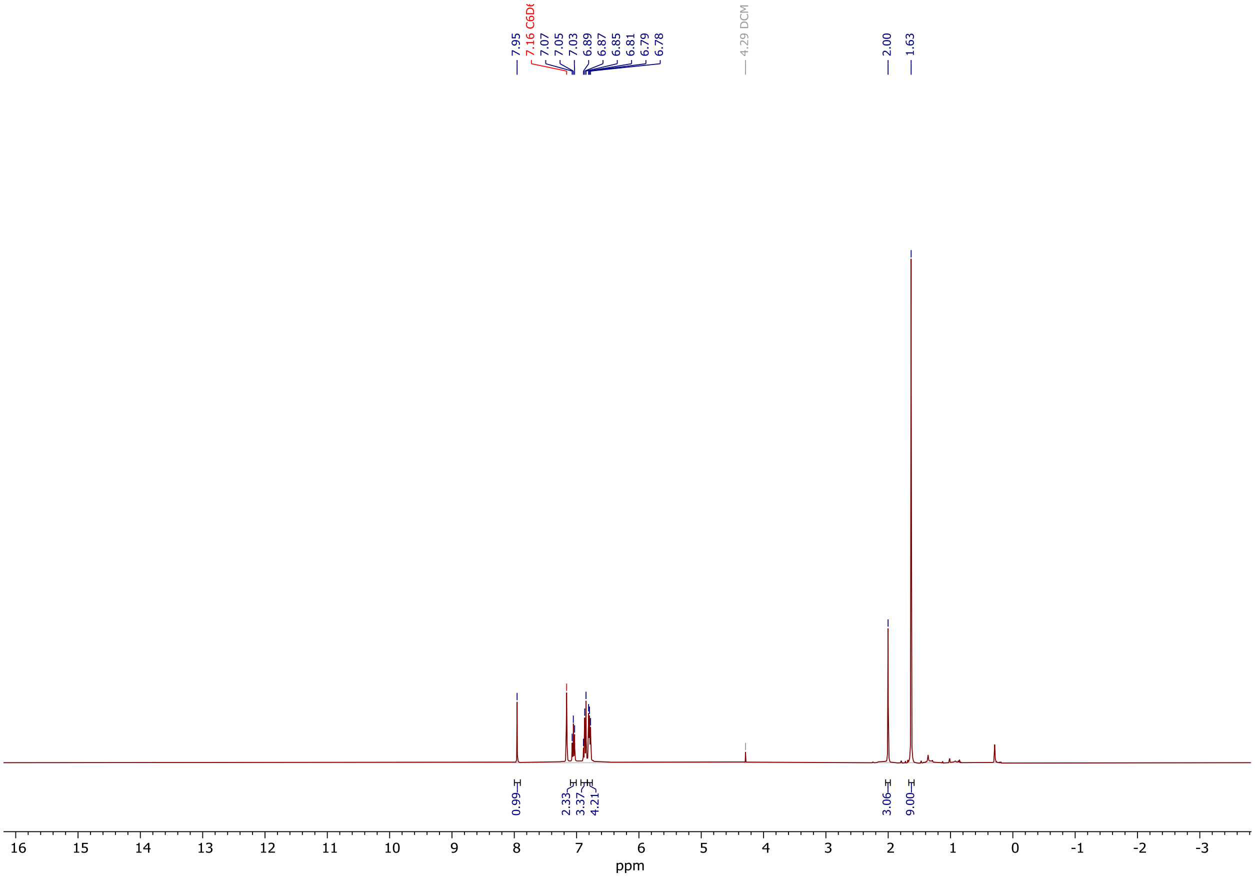


Figure S77. ^{1}H NMR spectrum of **5q** in C_6D_6.

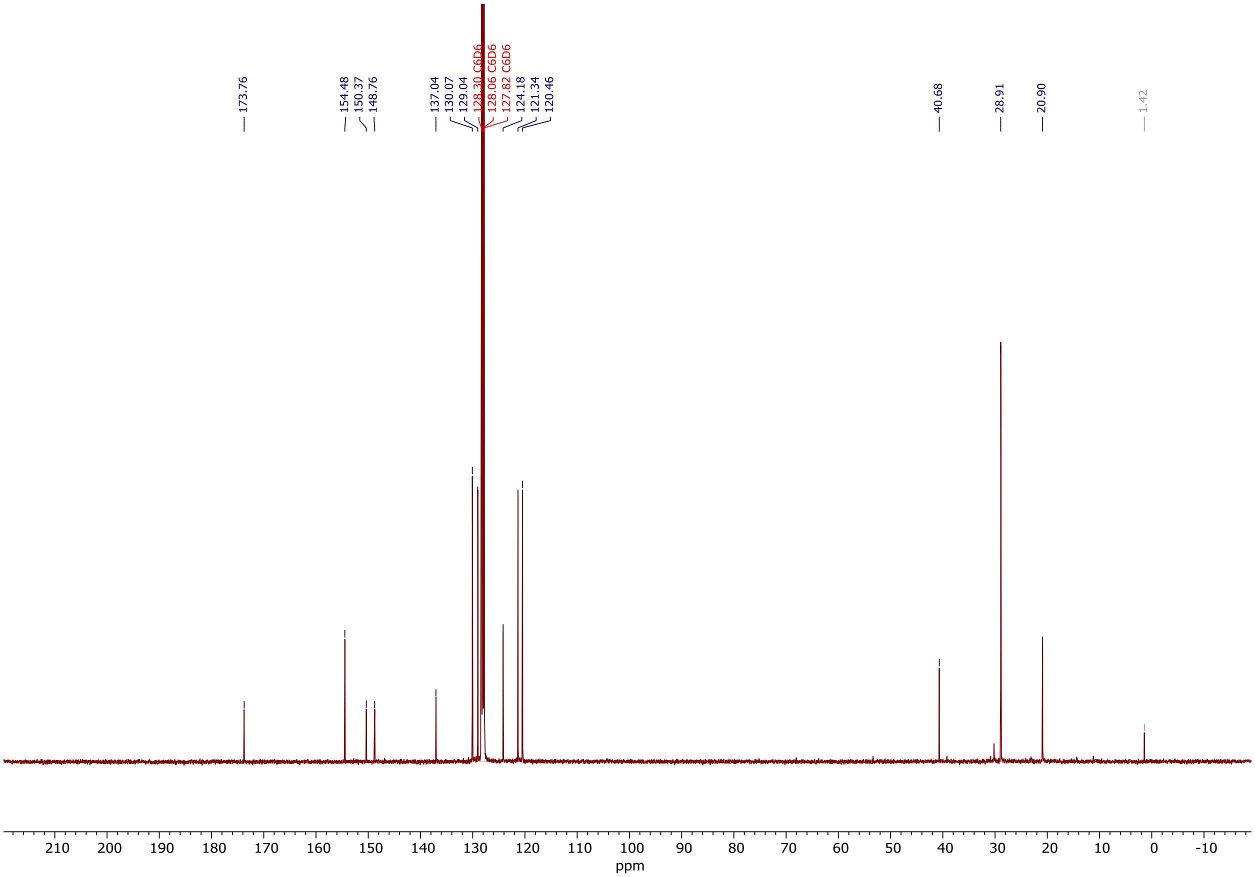
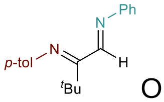


Figure S78. ^{13}C NMR spectrum of **5q** in C_6D_6.

(1E,2E)-3,3-dimethyl-*N*^{1}-phenyl-*N*^{2}-(p-tolyl)butane-1,2-diimine (**5r**)



Orange oil, 49.4 mg. 44% isolated yield. **^{1}H NMR (500 MHz, C_6D_6)** δ 7.95 (s, 1H, C*H*), 7.02 – 6.97 (m, 2H, CH(C*H*CH)$_2$CN), 6.93 – 6.89 (m, 3H, CH_3C(C*H*CH)$_2$CN & C*H*(CHCH)$_2$CN), 6.87 (d, *J* = 8.1 Hz, 2H, CH_3C(CHC*H*)$_2$CN), 6.77 (d, *J* = 8.2 Hz, 2H, CH(CHC*H*)$_2$CN), 2.04 (s, 3H, C*H*$_3$), 1.64 (s, 9H, C(C*H*$_3$)$_3$). **^{13}C NMR (126 MHz, C_6D_6)** δ 173.46, 155.72, 151.34, 147.59, 133.79, 129.68, 129.42, 127.04, 121.27, 120.77, 40.73, 28.91, 20.86. **ESI-HRMS (m/z):** calcd. for $C_{19}H_{22}N_2Na^+$, 301.1681; found, 301.1673. (diff. 0.0008).

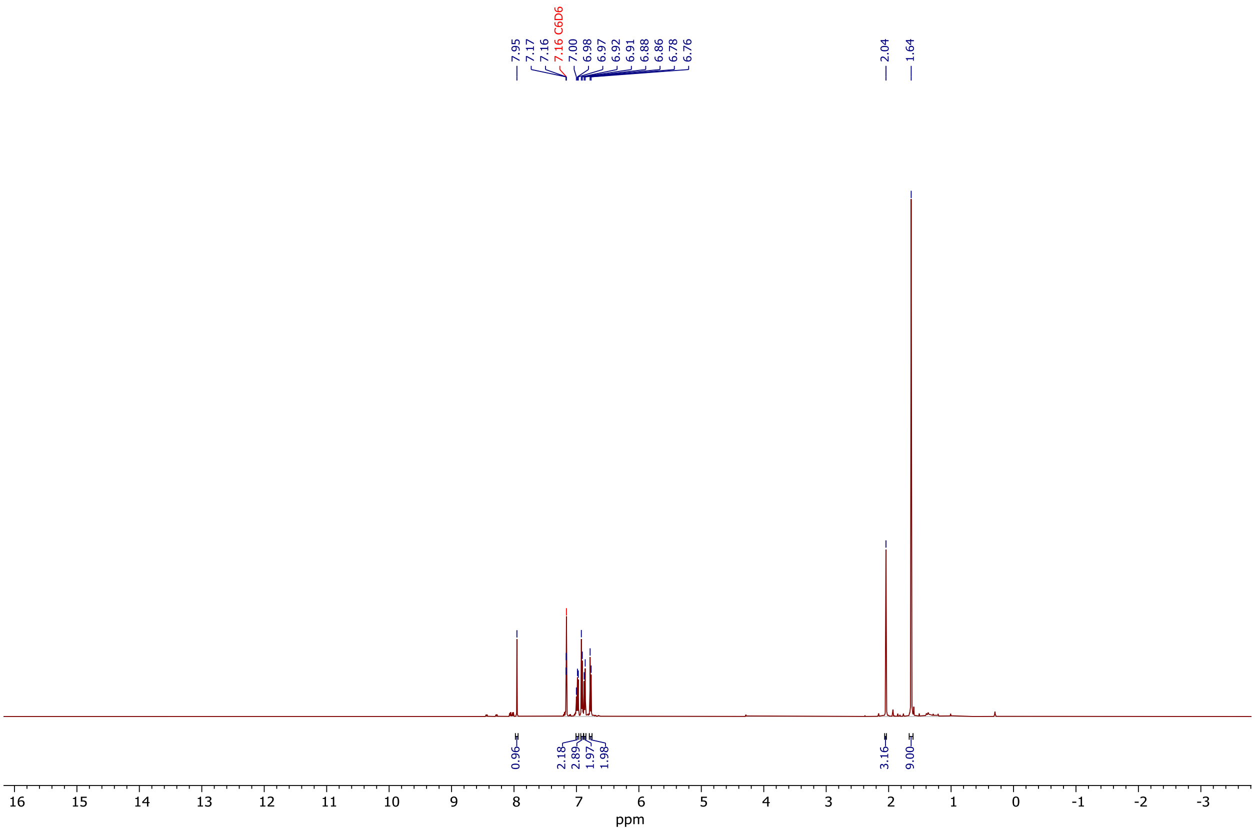


Figure S79. ^{1}H NMR spectrum of **5r** in C_6D_6.

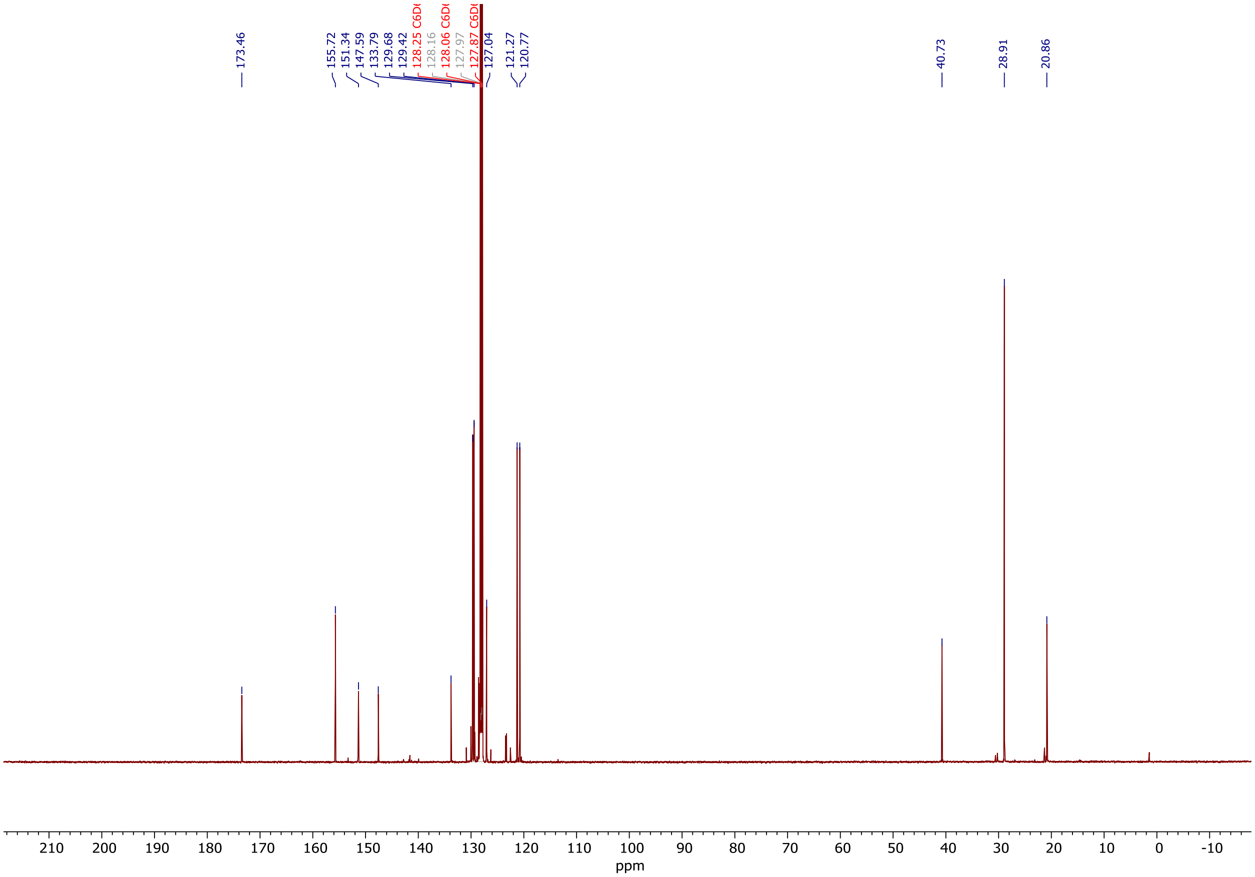
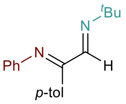


Figure S80. ^{13}C NMR spectrum of **5r** in C_6D_6.

N^2-(*tert*-butyl)-*N*^{1}-phenyl-1-(*p*-tolyl)ethane-1,2-diimine (**5s**)



Orange oil, 60.2 mg. Isolated as a mixture of diimine (50% yield) with some pyrrole impurity (4%) (92% pure). ^{1}H and ^{13}C NMR show a mixture of two major isomers in solution (C_6D_6). **ESI-HRMS (m/z):** calcd. for $C_{19}H_{22}N_2Na^+$, 301.1681; found, 301.1688. (diff. 0.0007).

^{1}H NMR (500 MHz, C_6D_6) (both isomers) δ 8.43, 8.29, 8.27, 7.91, 7.18, 7.16, 7.13, 7.11, 7.10, 7.07, 7.06, 7.03, 7.02, 7.00, 6.95, 6.94, 6.93, 6.91, 6.89, 6.88, 6.82, 6.80, 6.78, 6.77, 2.08, 1.89, 1.12, 1.01. **^{13}C NMR (126 MHz, C_6D_6)** (both isomers and pyrrole) ^{13}C NMR (126 MHz, C_6D_6) δ 167.36, 163.91, 158.93, 152.27, 151.25, 150.84, 140.84, 138.52, 135.06, 132.14, 131.21, 130.54, 130.19, 129.73, 129.34, 128.98, 128.94, 128.48, 128.35, 128.25, 128.06, 127.97, 127.87, 125.36, 124.32, 124.10, 121.18, 121.04, 58.88, 58.27, 31.84, 30.46, 30.22, 29.36, 29.04, 21.34, 21.16.

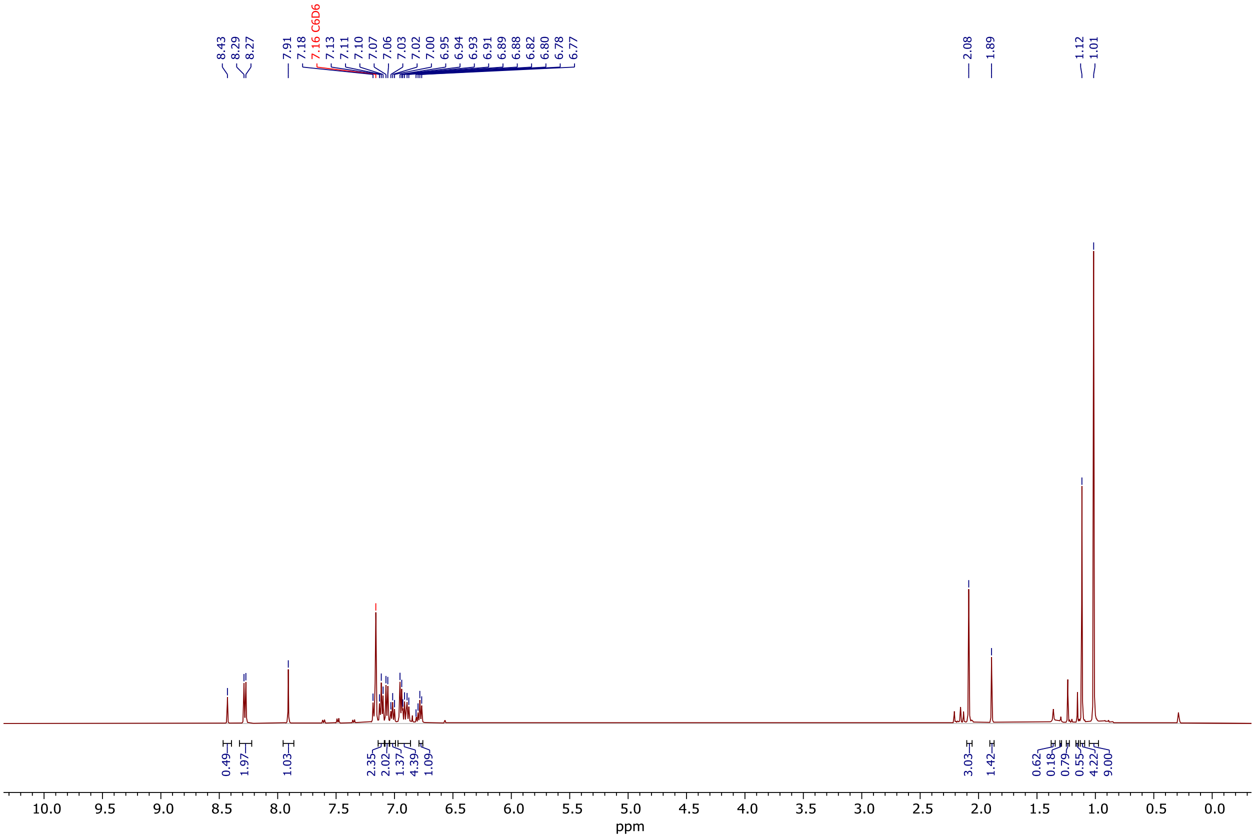


Figure S81. ^{1}H NMR spectrum of **5s** in C_6D_6.

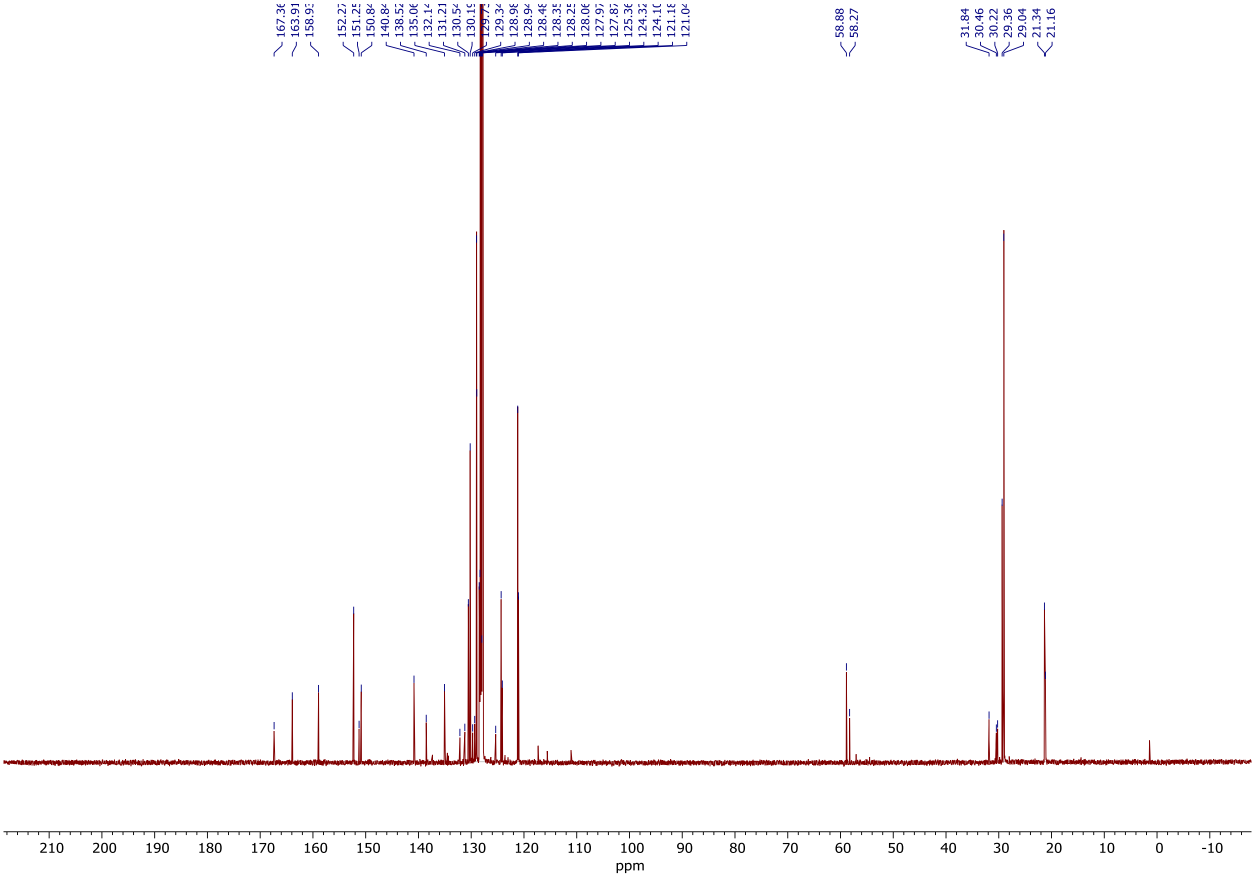
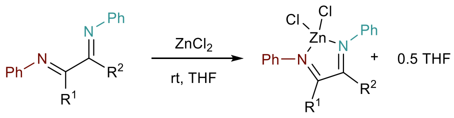


Figure S82. ^{13}C NMR spectrum of **5s** in C_6D_6.

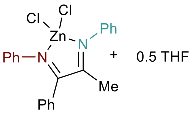
Addition of $ZnCl_2$ to asymmetric diimine isomers (Figure 3, **6f-6h, 6l**)



General procedure: 5 mL of THF was added to a 20 mL scintillon vial containing diimine (0.25 mmol), along with a stirbar. $ZnCl_2$ (0.25 mmol) in 5 mL THF was then added, and the reaction was stirred for 2 h at room temperature. The volatiles were reduced to obtain a brown powder, which was washed with hexanes and dried. A ^1H and ^{13}C NMR spectrum was then recorded in $CDCl_3$. Crystals suitable for XRD were grown from this $CDCl_3$ solution (Figure S97).

The resulting $ZnCl_2(diimine)\cdot 0.5THF$ complex was then washed with THF to remove the half equivalent of THF that was not able to be removed by vacuum (only demonstrated for 6f, Figure S83-84).

ZnCl$_2$((*1E,2E*)-*N*^{1},*N*^{2}-1-triphenylpropane-1,2-diimine)·0.5THF (**6f**)



Brown powder, 136.6 mg. 93% isolated yield. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.49 – 7.30 (m, 10H, Ar-*H*), 7.23 – 7.15 (m, 5H, Ar-*H*), 3.80 (s, 2H, 0.5 O(C*H*$_2$)$_2$(CH$_2$)$_2$), 2.20 (s, 3H, C*H*$_3$), 1.86 (s, 2H, O(CH$_2$)$_2$(C*H*$_2$)$_2$). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.38, 167.98, 143.85, 143.61, 131.63, 131.16, 129.95, 129.45, 129.40, 128.53, 128.53, 128.43, 123.72, 122.18, 68.75, 25.63, 21.35.

After THF wash **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.50 – 7.39 (m, 5H), 7.37 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.0 Hz, 2H), 7.23 – 7.10 (m, 5H), 2.19 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 168.93, 167.58, 143.94, 143.67, 131.71, 131.18, 129.95, 129.50, 129.40, 128.55, 128.45, 128.41, 123.73, 122.13, 77.41, 77.36, 77.16, 76.91, 21.28.

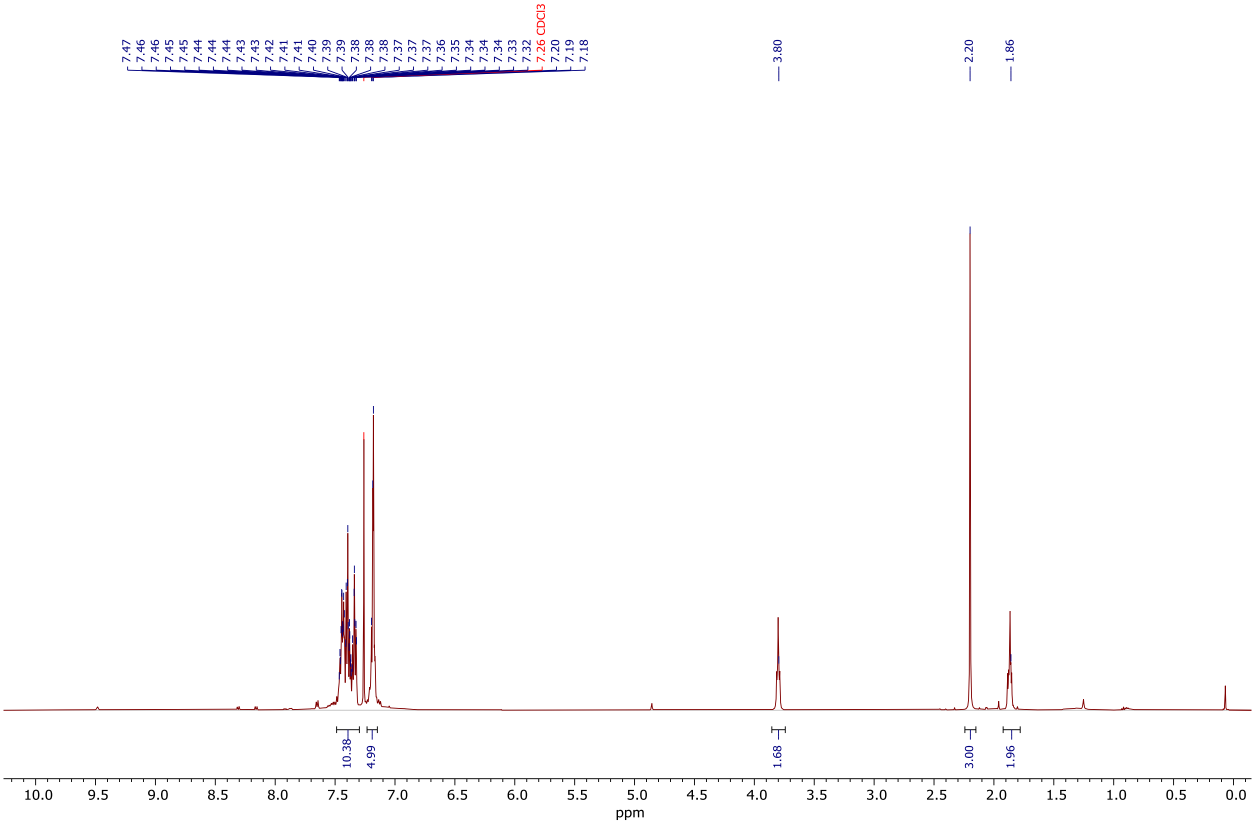


Figure S83. ^{1}H NMR spectrum of **6f** in CDCl$_3$.

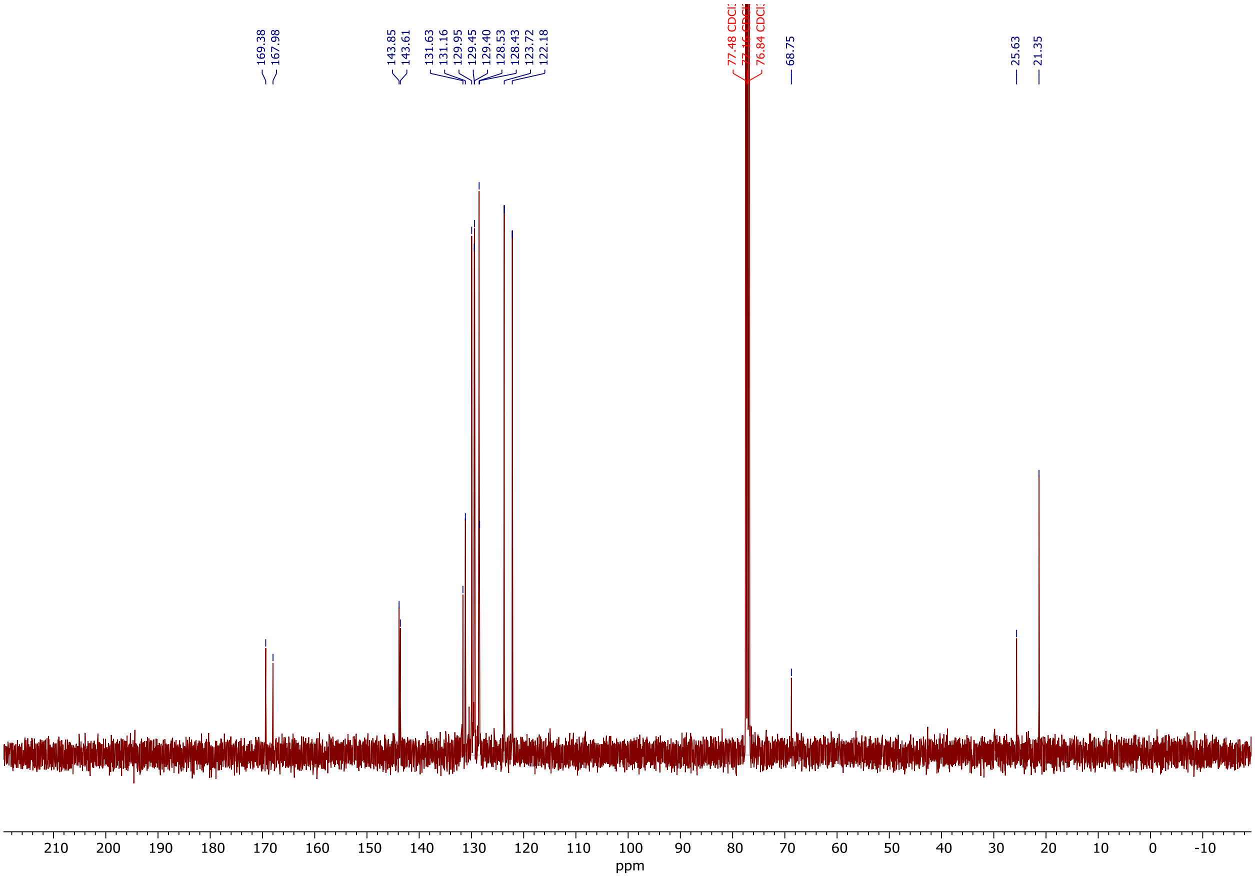


Figure S84. ^{13}C NMR spectrum of **6f** in $CDCl_3$.

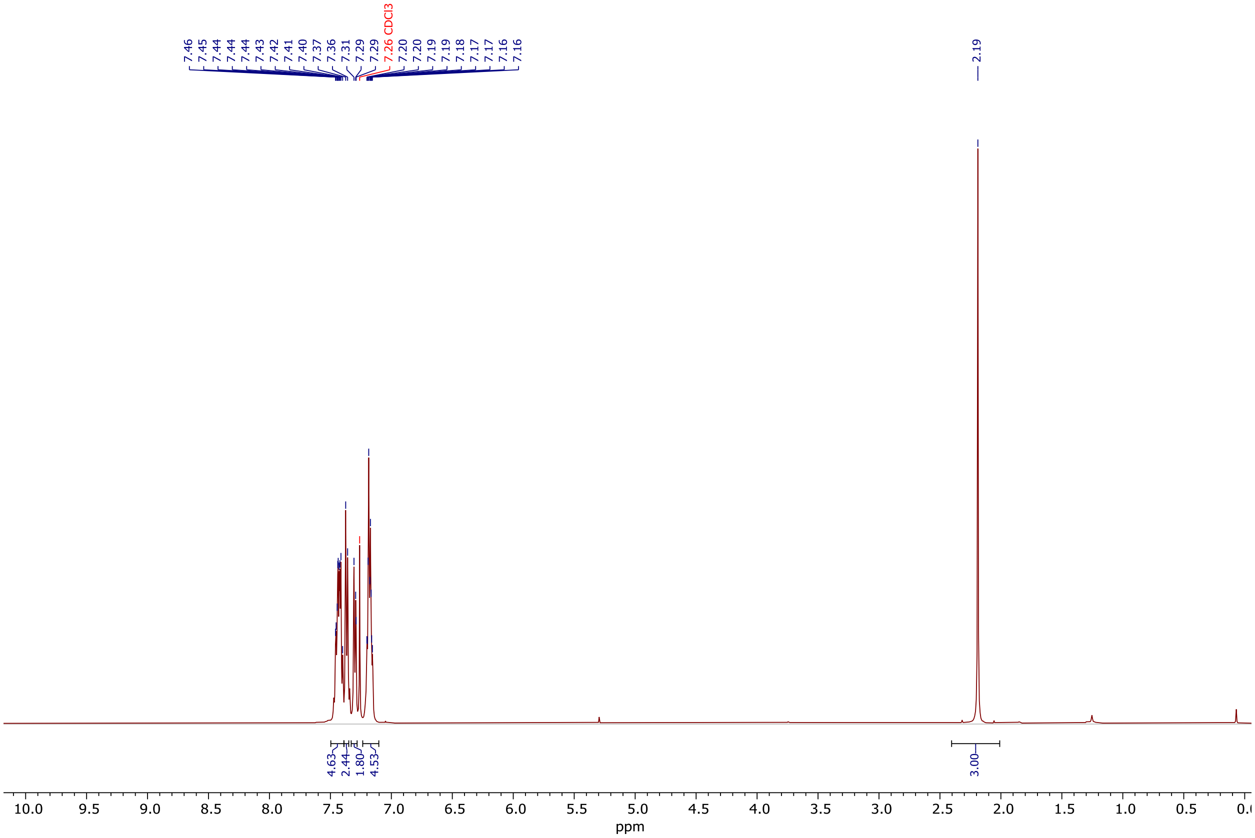


Figure S85. ^{1}H NMR spectrum of **6f** in $CDCl_3$ after THF wash.

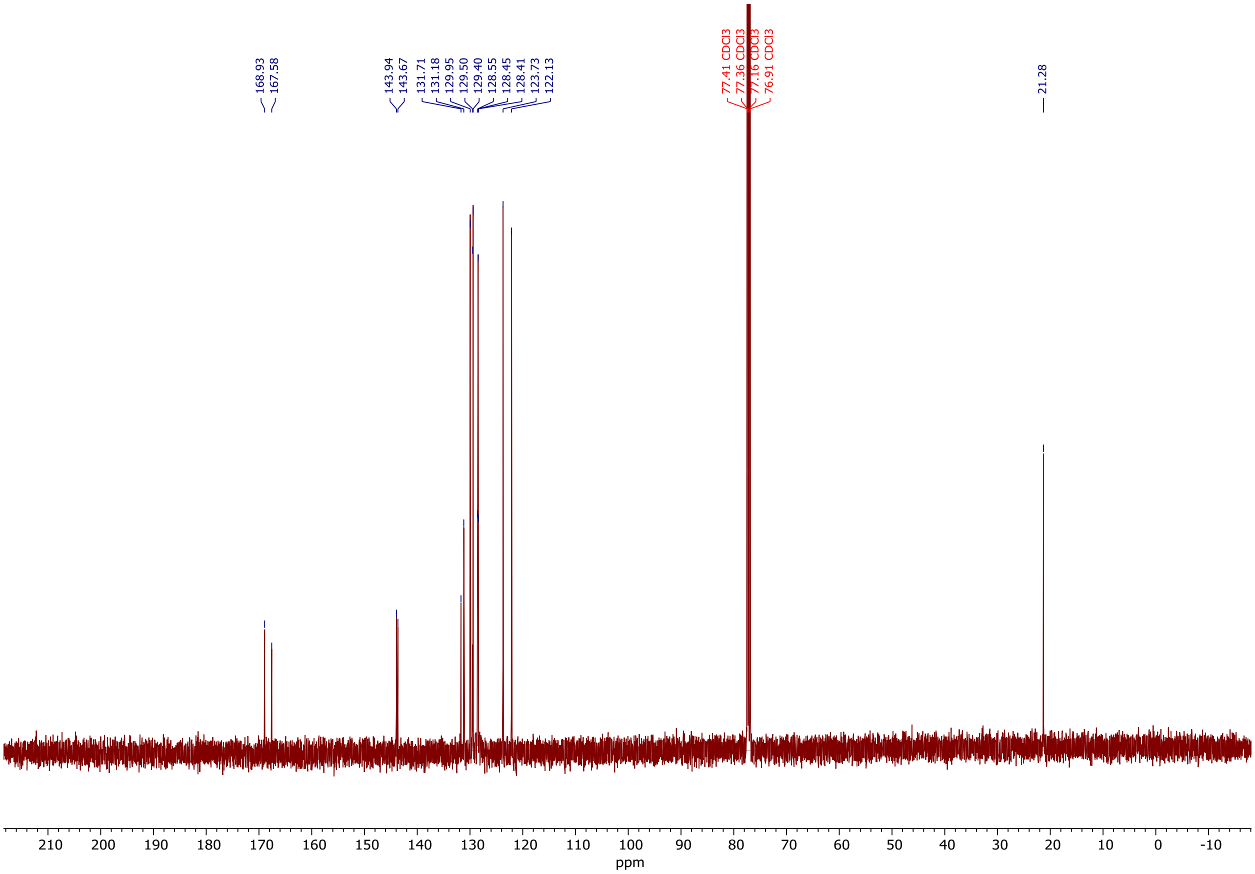
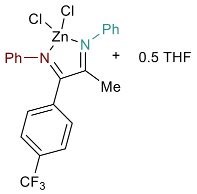


Figure S86. ^{13}C NMR spectrum of **6f** in $CDCl_3$ after THF wash.

$ZnCl_2$((*1E,2E*)-(4-trifluoromethyl)-N^1,N^2-diphenylpropane-1,2-diimine)·0.5THF (**6g**)



Light tan powder, 136.9 mg. 91% isolated yield. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67 (d, *J* = 8.1 Hz, 2H, $CF_3(CHCH)CC$), 7.52 (d, *J* = 8.1 Hz, 2H, $CF_3(CHCH)CC$), 7.44 – 7.39 (m, 2H, Ar-*H*), 7.39 – 7.34 (m, 3H, Ar-*H*), 7.23 – 7.17 (m, 3H, Ar-*H*), 7.16 – 7.10 (m, 2H, Ar-*H*), 3.83 – 3.68 (m, 2H, $O(CH_2)_2(CH_2)_2$), 2.16 (s, 3H, CH_3), 1.90 – 1.82 (m, 2H, $O(CH_2)_2(CH_2)_2$). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.05, 166.52, 143.61, 143.21, 135.29, 133.05 (q, *J* = 276.6 Hz), 129.86, 129.50, 129.16, 128.71, 128.39, 126.32 (q, *J* = 3.7 Hz), 123.31, 122.01, 68.05, 25.60, 21.20. (note, most of the CF_3 quartet (133.05) is buried in noise, and the ipso quartet was not observed).

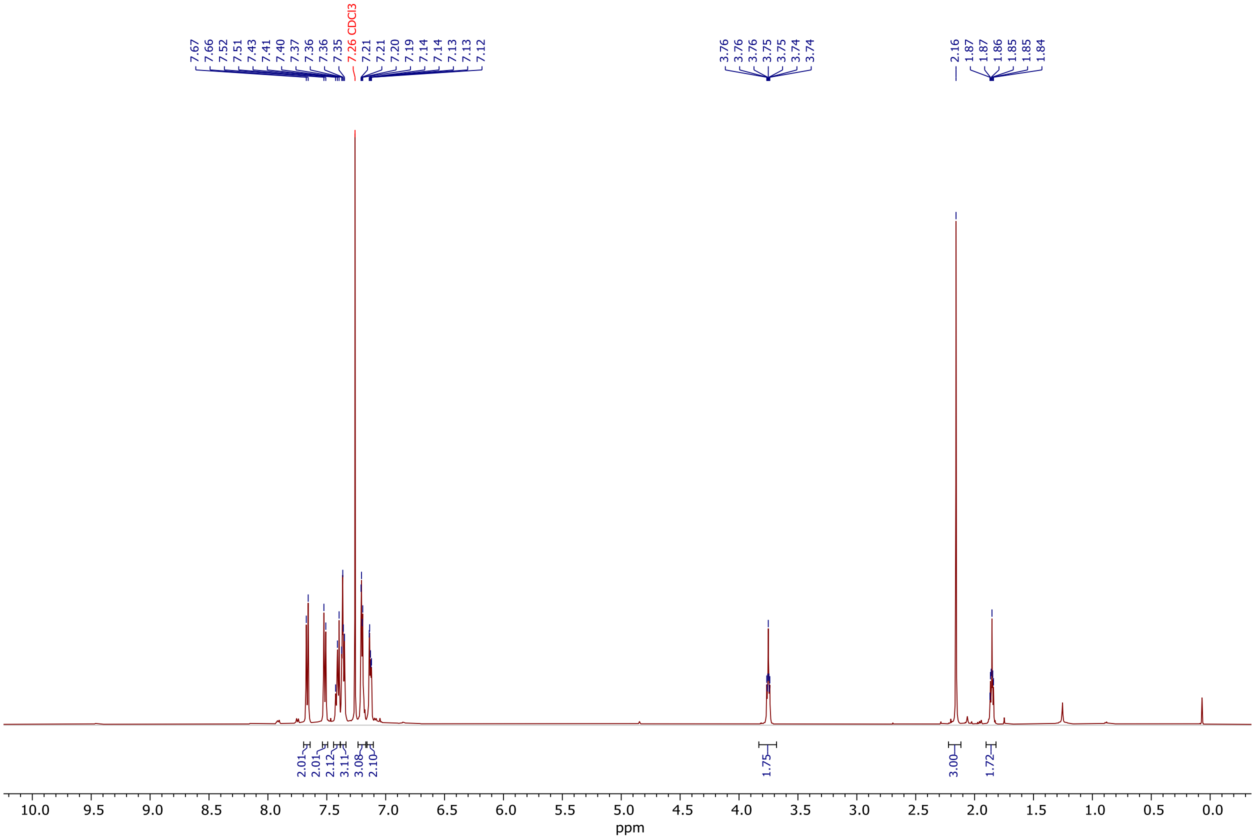


Figure S87. ^{1}H NMR spectrum of **6g** in $CDCl_3$.

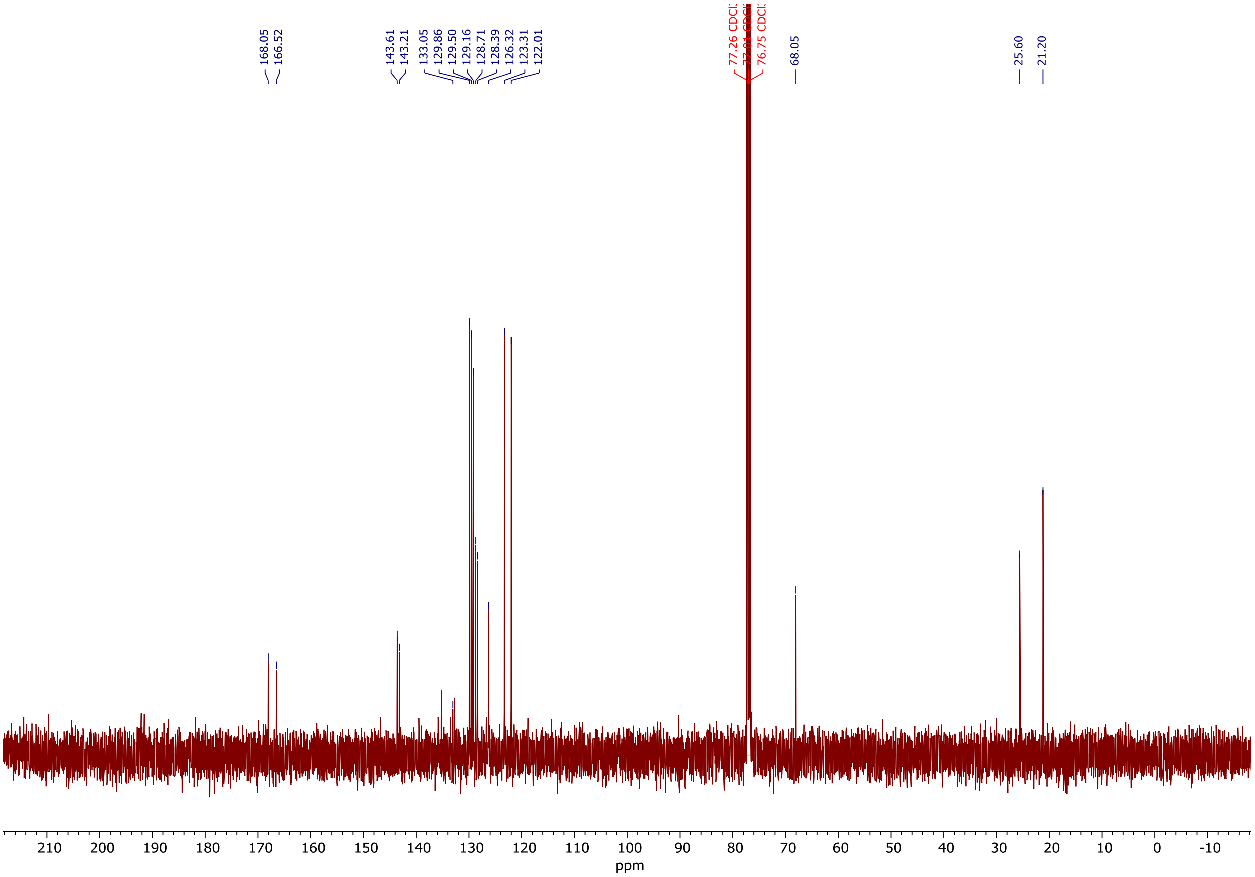


Figure S88. ^{13}C NMR spectrum of **6g** in $CDCl_3$.

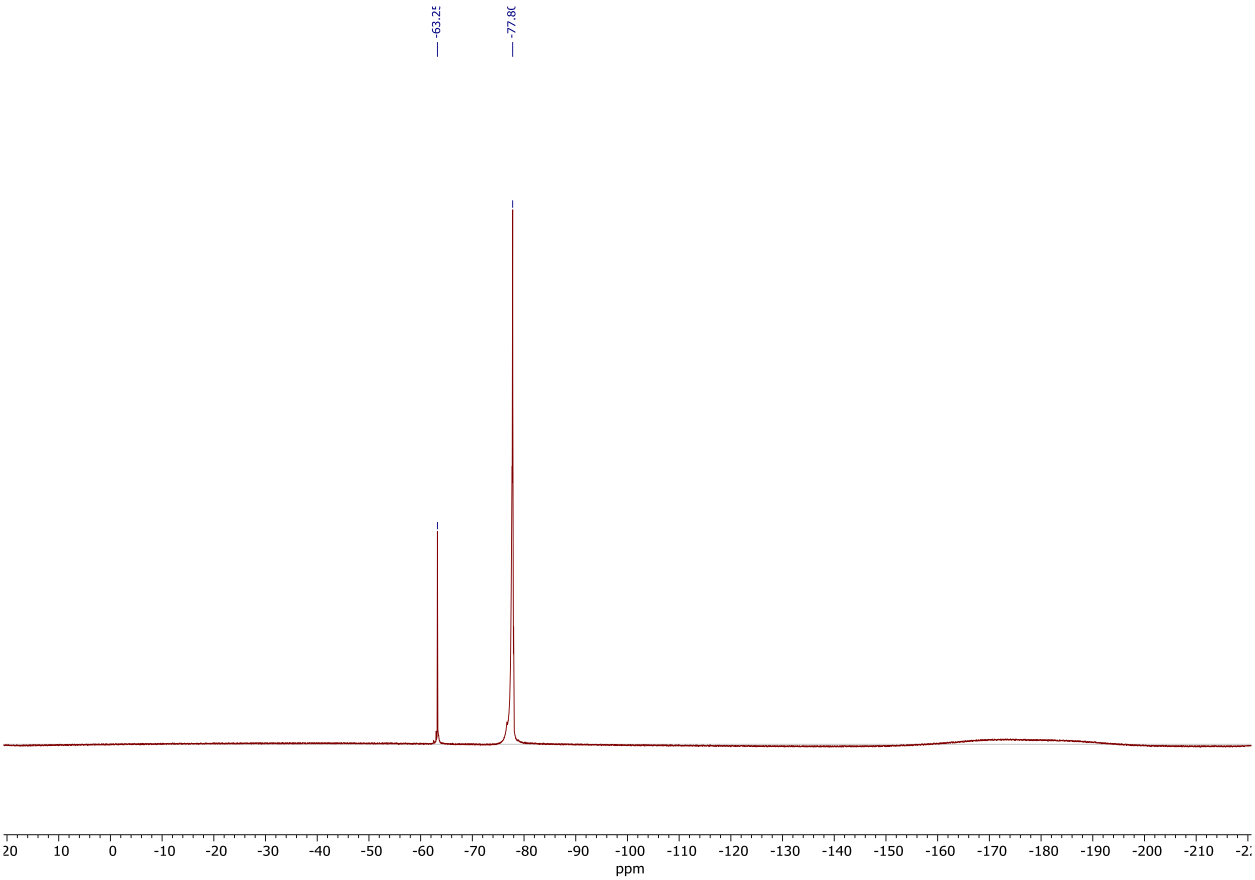
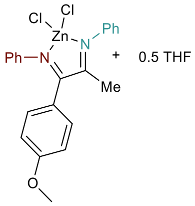


Figure S89. ^{19}F NMR spectrum of **6g** in $CDCl_3$ with trifluoroacetic acid (neat) reference capillary (δ -77.80).

$ZnCl_2$(*(1E,2E)*-(4-methoxyphenyl)-*N*^{1},*N*^{2}-diphenylpropane-1,2-diimine)·0.5THF (**6h**)



Brown powder, 117.8 mg. 93% isolated yield. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 – 7.42 (m, 2H, Ar-*H*), 7.41 – 7.32 (m, 3H, CHC(CHC*H*)CNCCH$_3$ & Ar-*H*), 7.22 (d, *J* = 8.5 Hz, 4H, CH$_3$OC(CHC*H*)CC & Ar-*H*), 7.21 – 7.15 (m, 3H, CHC(CHC*H*)CN & Ar-*H*), 6.90 (d, *J* = 8.9 Hz, 2H, CH$_3$OC(C*H*CH)CC), 3.82 (s, 3H, OC*H$_3$*), 3.79 – 3.75 (m, 2H, O(C*H$_2$*)$_2$(CH$_2$)$_2$), 2.23 (s, 3H, C*H$_3$*), 1.88 – 1.84 (m, 2H, O(CH$_2$)$_2$(C*H$_2$*)$_2$). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.62, 167.42, 161.71, 144.05, 143.98, 130.64, 129.95, 129.49, 128.37, 128.36, 123.77, 123.29, 122.12, 114.95, 68.35, 55.59, 25.72, 21.36.

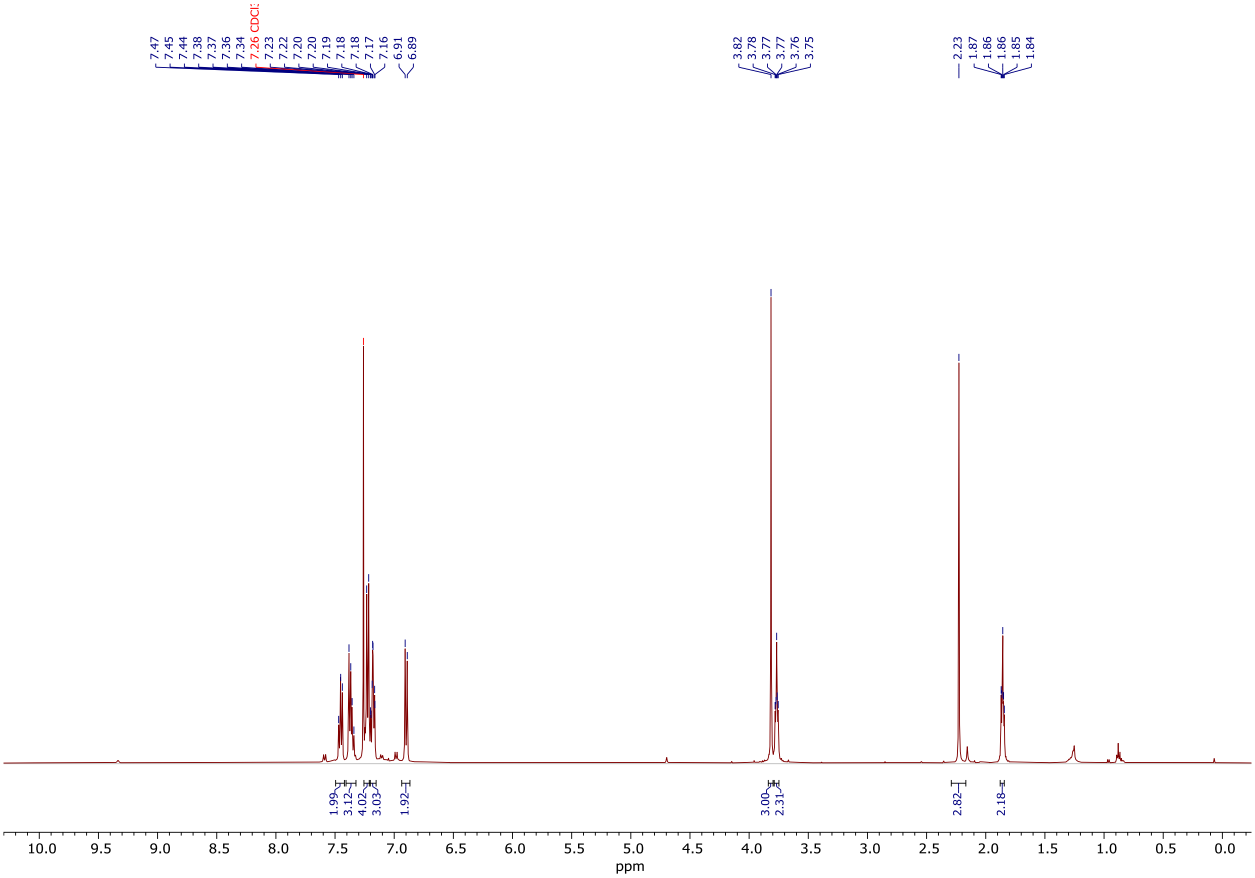


Figure S90. ^{1}H NMR spectrum of **6h** in $CDCl_3$.

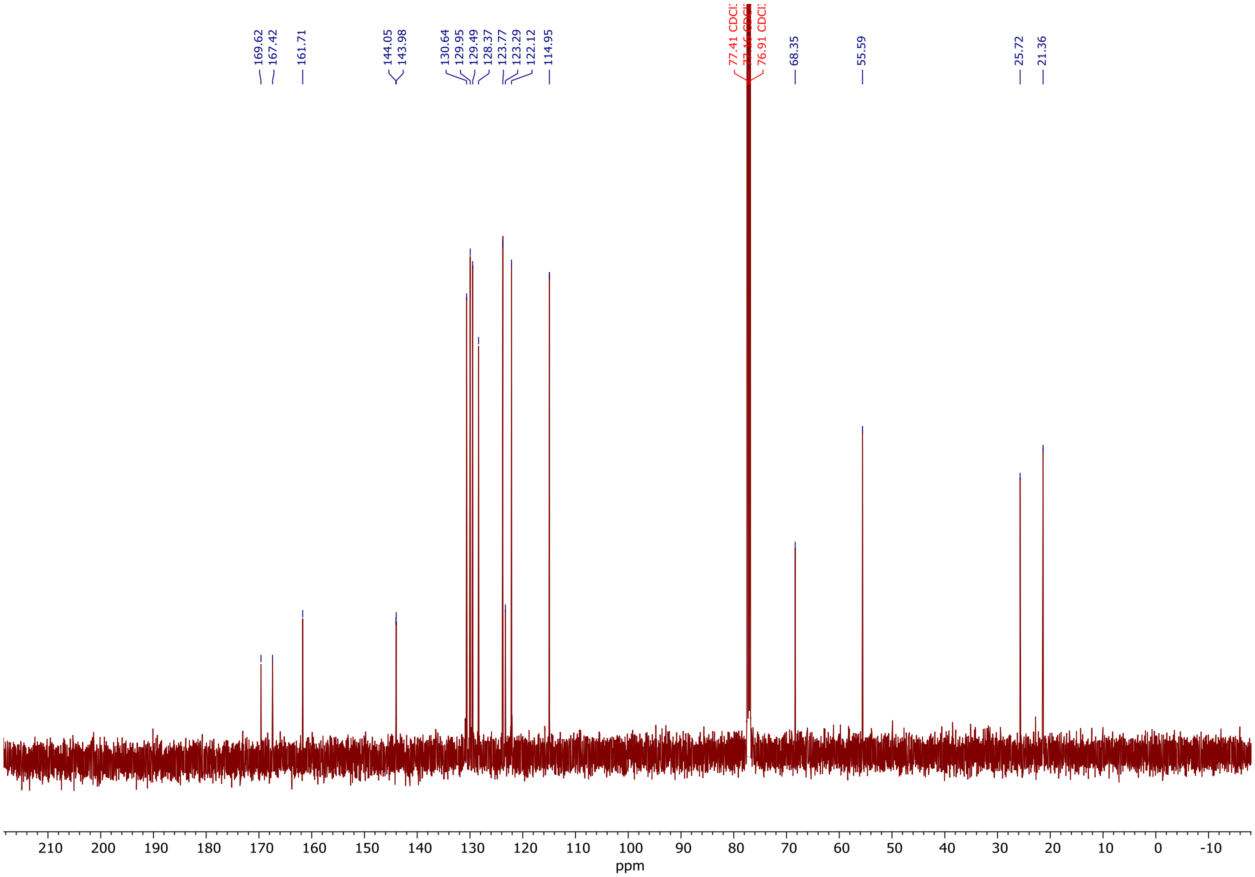
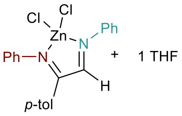


Figure S91. ^{13}C NMR spectrum of **6h** in $CDCl_3$.

ZnCl$_2$(*(1E,2E)-N^1*,*N^2*-diphenyl-1-(p-tolyl)ethane-1,2-diimine)·1THF (**6l**)



Brown powder, 114.8 mg. 86% isolated yield (some pyrrole impurity remaining). **^{1}H NMR (500 MHz, CDCl3)** δ 8.69 (s, 1H, C*H*), 7.88 – 7.78 (m, 2H, CH$_3$(CHC*H*)$_2$C), 7.61 – 7.51 (m, 3H, Ar-*H*), 7.35 – 7.27 (m, 7H, Ar-*H*), 7.25 – 7.24 (m, 2H, Ar-*H*), 3.87 – 3.66 (m, 4H, O(C*H$_2$*)$_2$(CH$_2$)$_2$), 2.41 (s, 3H, C*H*$_3$), 1.99 – 1.76 (m, 4H, O(CH$_2$)$_2$(C*H$_2$*)$_2$). **^{13}C NMR (101 MHz, CDCl3)** δ 162.18, 155.67, 143.99, 143.71, 143.19, 132.24, 130.56, 130.52, 129.92, 129.21, 128.92, 128.76, 123.62, 123.54, 77.48, 77.16, 76.84, 68.31, 25.72, 21.91.

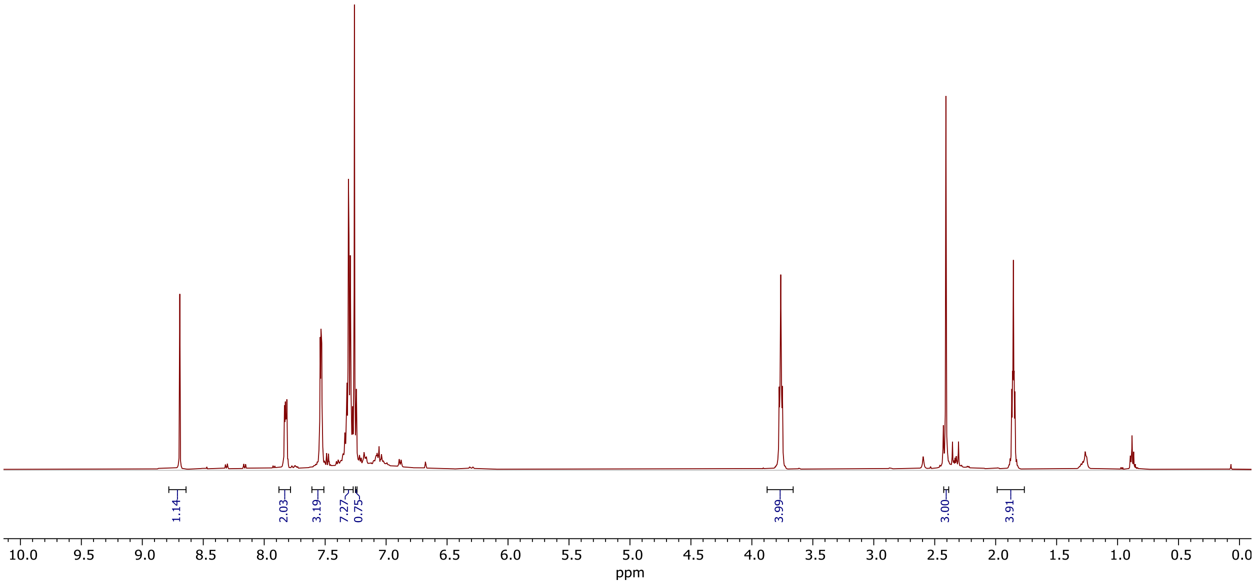


Figure S92. ^{1}H NMR spectrum of **6l** in CDCl$_3$.

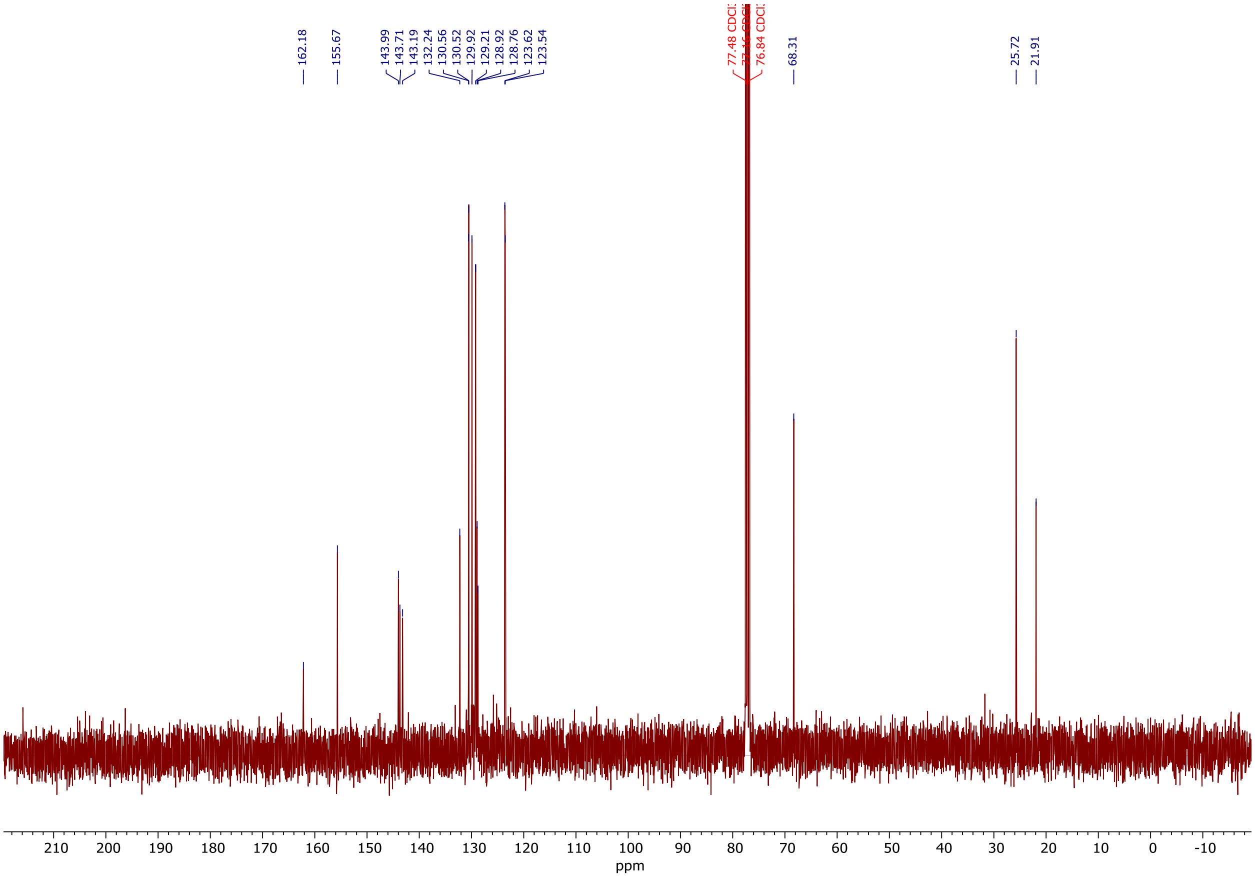
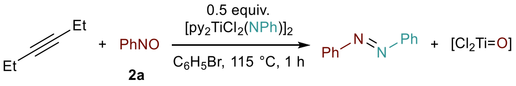


Figure S93. ^{13}C NMR spectrum of **6l** in CDCl$_3$.

Control reaction with [py$_2$TiCl$_2$NPh]$_2$, 3-hexyne, and PhNO



Procedure: [py$_2$TiCl$_2$(NPh)]$_2$ (17.6 mg, 0.048 mmol, 1 equiv.) and 0.5 mL of 0.020 M TMB in PhBr were added to an NMR tube, followed by 3-hexyne (4.8 mg, 0.059 mmol, 1 equiv.) and nitrosobenzene (5.5 mg, 0.050 mmol, 1 equiv.). The tube was capped, sealed with electrical tape, and heated to 115 ˚C in an oil bath for 1 hour. A ^{1}H NMR spectrum was recorded. Azobenzene formation was observed without formation of any diimine.

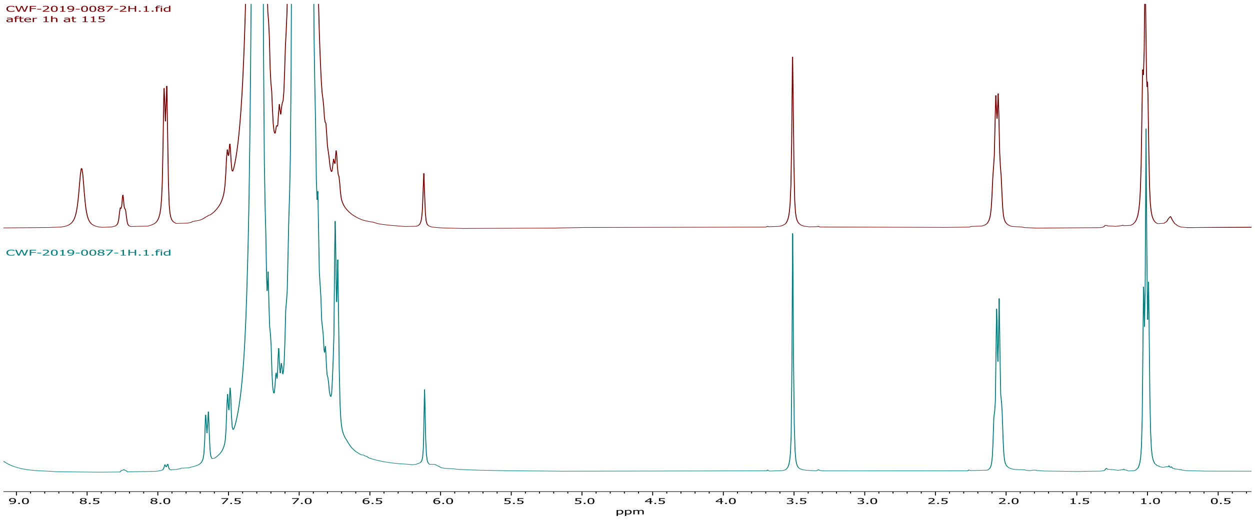
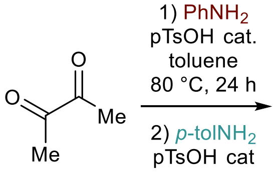


Figure S94. No-D ^{1}H NMR spectrum in PhBr showing (bottom) 3-hexyne and TMB, (top) azobenzene formation and unreacted 3-hexyne after 1 hr of heating at 115 °C.

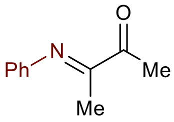
Evaluation of *in situ* sequential condensations from diketones



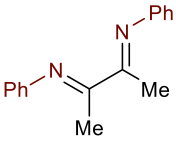
Symmetrical diimine - 2,3-butanedione

Procedure: 2,3-butanedione (86.1 mg, 1.0 mmol), aniline (93.1 mg, 1.0 mmol, 1.0 equiv.), and 1-2 mg of p-toluenesulfonic acid (p-TsOH) was added to a 20 mL scintillation vial with 10.0 mL of dry toluene and 43.0 mg of 1,3,5-trimethoxybenzene as an internal standard. The yellow-orange solution was allowed to stir at 80 °C for 24 h. An aliquot of the dark red solution was extracted for analysis by GC-FID. p-Toluidine (107 mg, 1.0 mmol, 1.0 equiv.) and another 1-2 mg of p-TsOH was added and the reaction was stirred for an additional 24 h at 80 °C. A second aliquot was extracted for GC-FID analysis.

Analysis of reaction mixture after step 1 (yields vs. TMB internal standard):



84%



5%

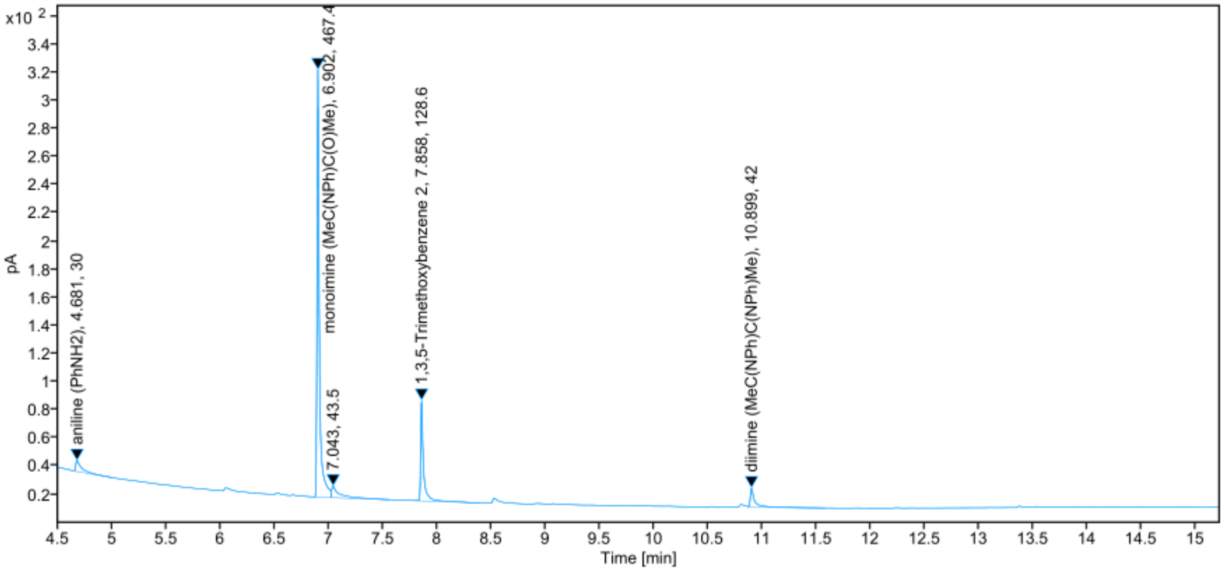
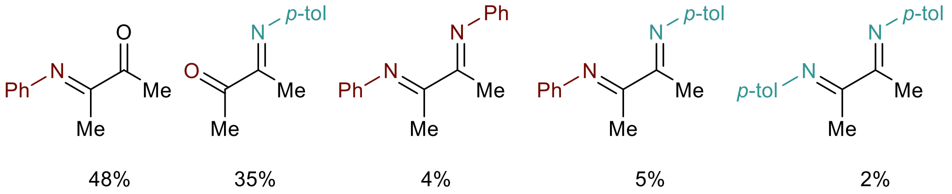


Figure S95. GC-FID of aliquot from reaction mixture 24 h following addition of aniline of 2,3-butanedione at 80 °C in toluene

Analysis of reaction mixture after step 2 (yields vs. TMB internal standard):



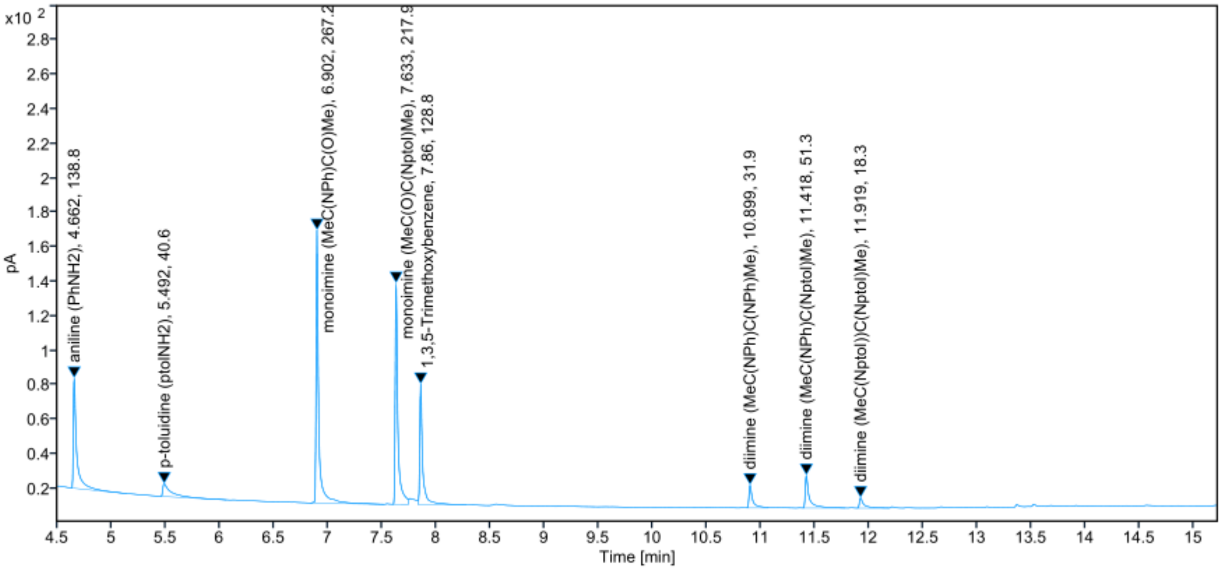
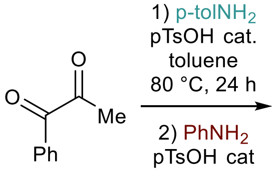


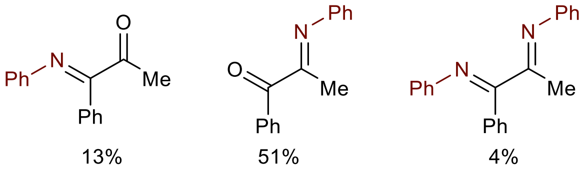
Figure S96. GC-FID of aliquot from reaction mixture 24 h following second condensation step.

Unsymmetrical diimine - 1-phenyl-1,2-propanedione



Procedure: 1-phenyl-1,2-propanedione (148.0 mg, 1.0 mmol), aniline (93.1 mg, 1.0 mmol, 1.0 equiv.), and 1-2 mg of p-toluenesulfonic acid (p-TsOH) was added to a 20 mL scintillation vial with 10.0 mL of dry toluene and 43.0 mg of 1,3,5-trimethoxybenzene as an internal standard. The reaction was allowed to stir at 80 °C for 24 h. An aliquot was extracted for analysis by GC-FID. p-Toluidine (107 mg, 1.0 mmol, 1.0 equiv.) and another 1-2 mg of p-TsOH was added and the reaction was stirred for an additional 24 h at 80 °C. A second aliquot was extracted for GC-FID analysis.

Analysis of reaction mixture after step 1 (yields vs. TMB internal standard):



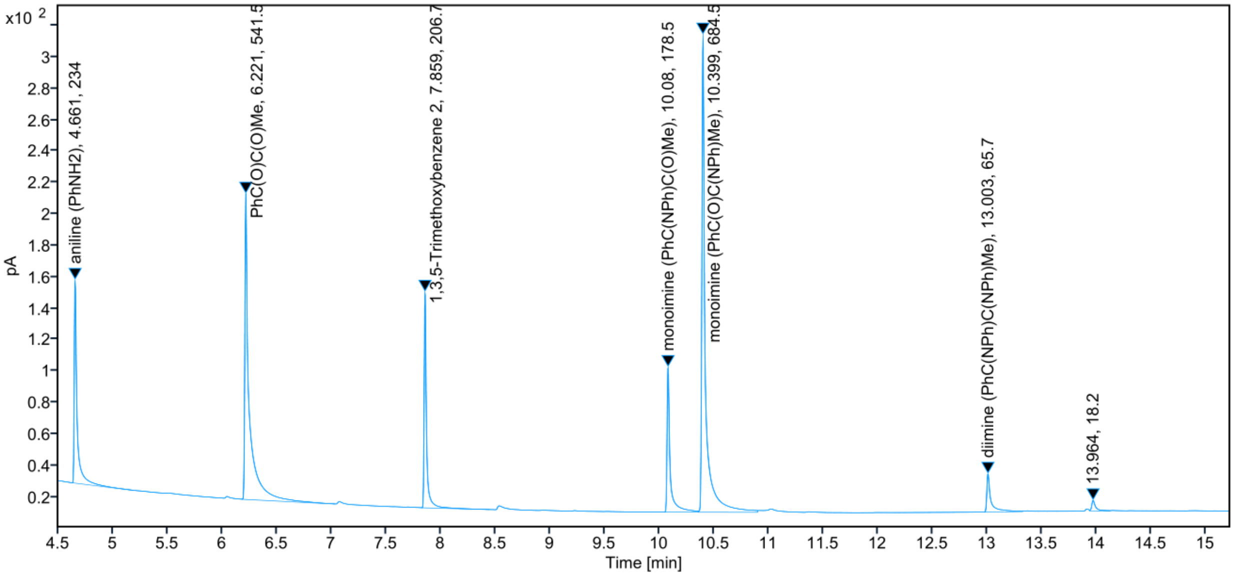
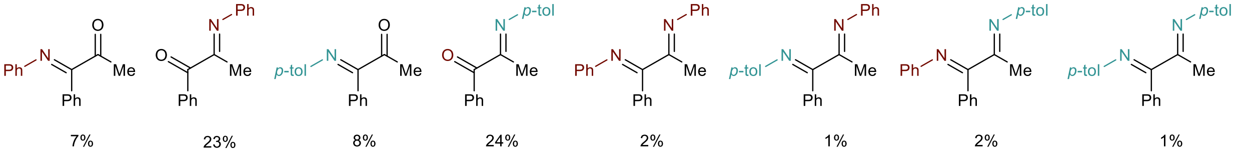


Figure S97. GC-FID of aliquot from reaction mixture 24 h following addition of p-toluidine of 1-phenyl-1,2-propanedione at 80 °C in toluene.

Analysis of reaction mixture after step 2 (yields vs. TMB internal standard)



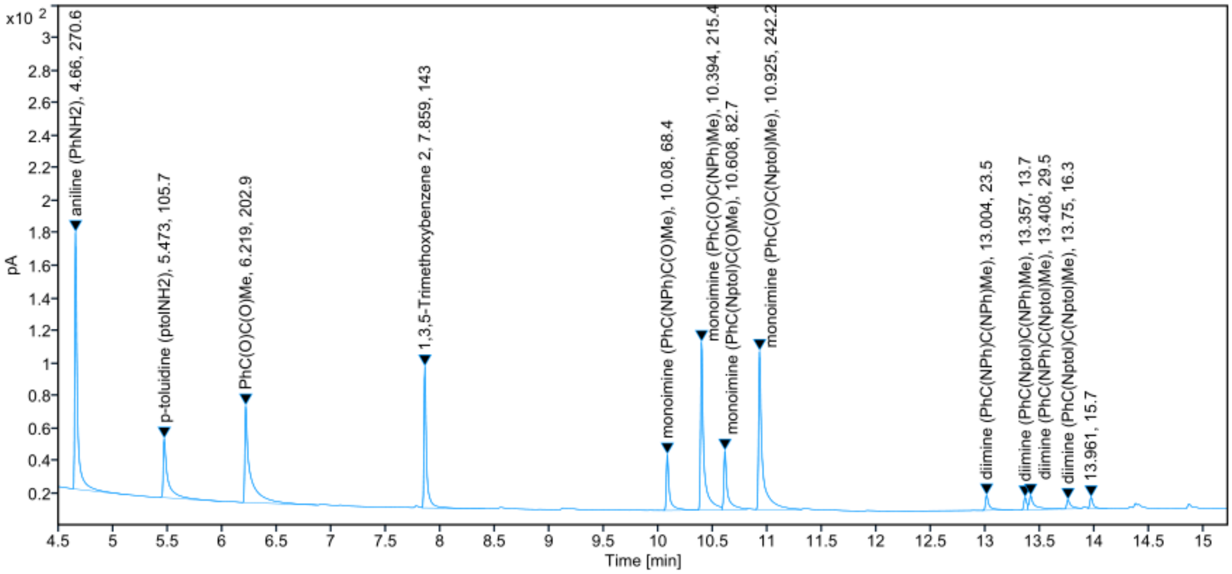


Figure S98. GC-FID of aliquot from reaction mixture 24 h following second condensation step.

XRD Data

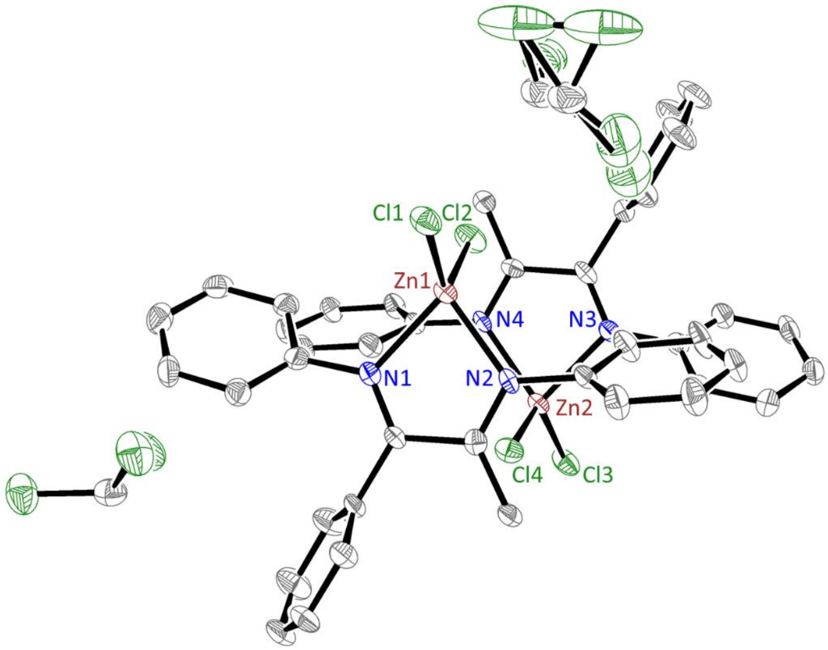


Figure S99. ORTEP diagram of **6f**. Thermal ellipsoids are drawn at 50% probability.

	6f
CCDC Number	2072232
Empirical Formula	$C_{21}H_{18}Cl_2N_2Zn$ ($CDCl_3$)
Formula Weight	554.01
Temperature (K)	125(2)
a, Å	23.376(2)
b, Å	10.6352(9)
c, Å	20.2506(19)
α, °	90
β, °	106.848(4)
γ, °	90
Volume, Å^3	4818.4(8)
Z	8
Crystal System	Monoclinic
Space Group	$P2_1/c$
$d_{calc,}$ g/cm^3	1.527
θ Range, °	2.034 to 27.944
μ, mm^{-1}	1.586
Abs. Correction	Multi-scan
GooF	1.053
$R_1{}^a$	0.0687
$wR_2{}^b$ [I>2σ(I)]	0.1758

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$.

[b] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Computational Methods

The employed computational methods were adapted from previous work on similar systems.[4, 11] All geometry optimizations and frequency calculations were performed with the Gaussian 16 package (Rev. C.016).[12] Structures were optimized using the M06 functional[13] with 6-311G(d,p)[14] as a basis set. A SMD continuum solvation model[15] for bromobenzene was used for the best approximation of the experimental conditions. The ultrafine grid setting was used for all calculations to avoid integration errors, as is suggested with M06 functionals.[16-17] Frequency calculations were performed on the optimized geometries at the same level of theory to obtain free energies and verify the structure as either a minima with no imaginary frequencies or as a transition state with a single imaginary frequency. To mitigate fictitious contributions by small frequencies, thermal energies were calculated at 298.15 K and 1 atm using a frequency correction calculation that scales any frequencies lower than 50 cm^{-1} to 50 cm^{-1}.[18] A graphical representation as well as the cartesian coordinates for all optimized geometries are given below with their electronic and free energy (before and after the frequency correction). A sample Gaussian input file with the settings described above has also been provided.

Intrinisic bond orbital (IBO) calculations were performed with MOLPRO 2019[19-20] and visualized with IBOView.[21-22] All calculations were performed with the M06 functional[13] and def2-TZVP basis set[23] (IBOView does not support the previous used 6-31G-family of basis sets). Density fitting with def2-TZVP JK-fitting was used to accelerate MOLPRO calculations.

Sample Gaussian input:

```
# opt=(CalcFC) freq m06/6-311g(d,p) integral(grid=ultrafinegrid)
SCRF(SMD,Solvent=Bromobenzene) Temperature=298.15

PhNO

0 1
C      0.550971     -0.219292     -0.000020
C     -0.333310     -1.292700     -0.000010
C     -1.697780     -1.052119      0.000010
C     -2.159348      0.257752      0.000020
C     -1.267677      1.331301     -0.000010
C      0.092483      1.097859     -0.000030
H     -1.647025      2.348151     -0.000010
H      0.815324      1.907118     -0.000030
H      0.076198     -2.298761     -0.000020
H     -2.400101     -1.878988      0.000040
H     -3.227918      0.450544      0.000050
N      1.935581     -0.576234     -0.000030
O      2.715302      0.346095      0.000050
```

Intrinsic bond orbital analysis

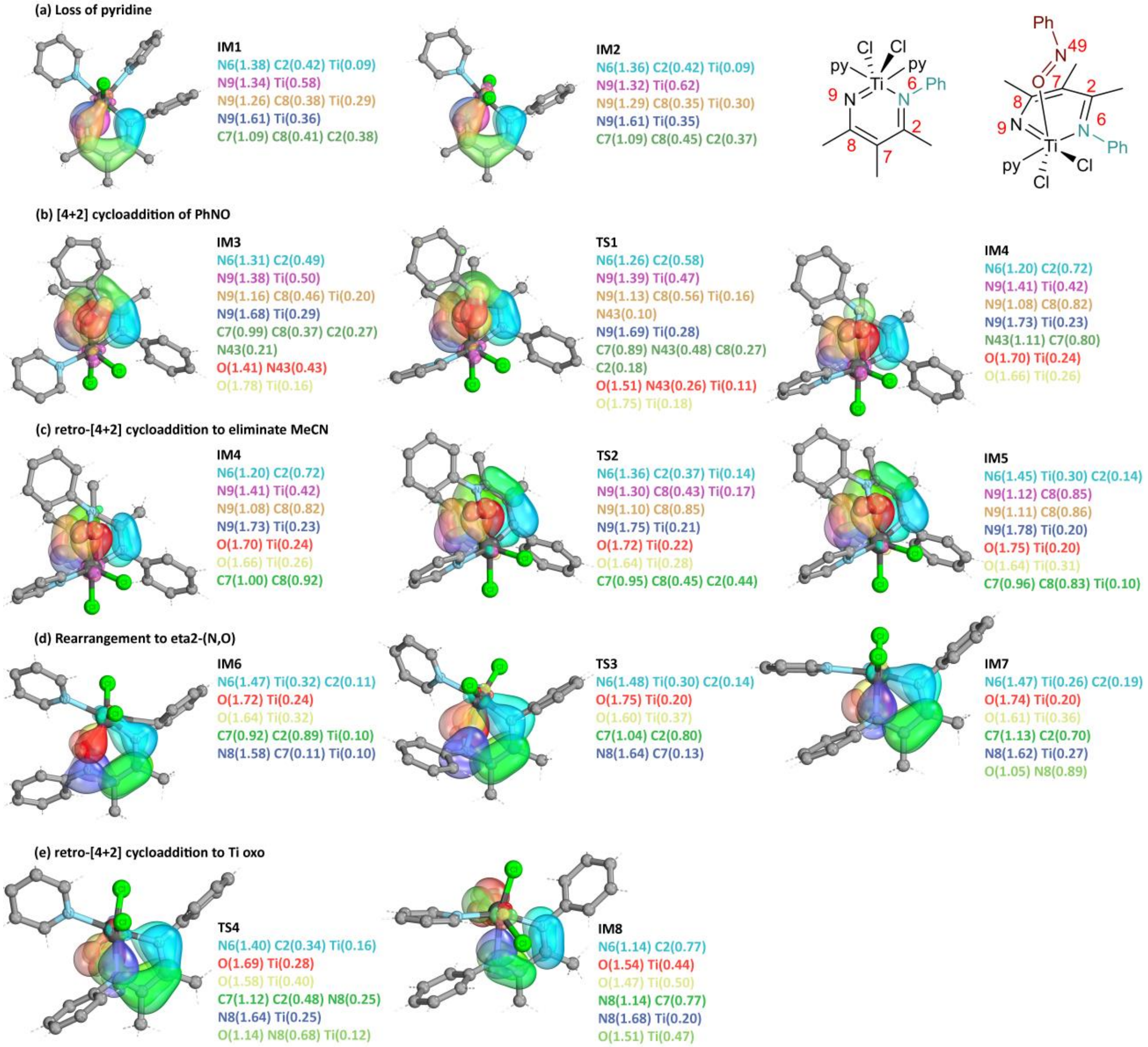


Figure S100. Relevant IBOs for intermediates and transition states of each reaction step (**IM1 to IM8**) are shown. The fraction of electrons in doubly occupied orbitals assigned to each atom are given in parenthesis (contributions that are ≤0.10 are omitted). Atom number labels correspond to line positions in respective cartesian coordinates (xyz).

Sample Molpro input:

```
memory,200,m;

geometry={
C        0.550971       -0.219292       -0.000020
C       -0.333310       -1.292700       -0.000010
C       -1.697780       -1.052119        0.000010
C       -2.159348        0.257752        0.000020
C       -1.267677        1.331301       -0.000010
C        0.092483        1.097859       -0.000030
```

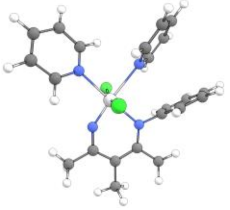
```
H     -1.647025      2.348151     -0.000010
H      0.815324      1.907118     -0.000030
H      0.076198     -2.298761     -0.000020
H     -2.400101     -1.878988      0.000040
H     -3.227918      0.450544      0.000050
N      1.935581     -0.576234     -0.000030
O      2.715302      0.346095      0.000050
}

basis=def2-TZVP
{df-rks,XC-m06,maxit=100; save, 2101.2}
{ibba,MAXIT_IB=100; orbital,2101.2; save,2103.2}
{put,xml,'PhNO.xml'; orbital,2103.2; keepspherical; skipvirt}
```

XYZ coordinates (Å) of optimized structures with electronic, free, and frequency corrected free energies (a.u.) at 298.15 K and 1 atm using M06/6-311g(d,p)/ultrafine in bromobenzene

IM1

Electronic energy: -2841.319854
Gibbs free energy: -2840.967609
Corrected free energy: -2840.965493

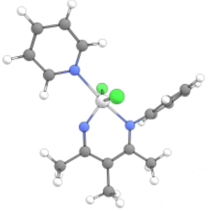


53
IM1

C	-3.683846	2.083034	-0.309210
C	-2.194348	2.041263	-0.115765
H	-3.914039	2.161545	-1.379911
H	-4.120392	2.957348	0.177675
H	-4.186224	1.194244	0.069535
N	-1.585024	0.871185	0.081737
C	-1.522072	3.294750	-0.161781
C	-0.161054	3.379911	0.146809
N	0.530016	2.281541	0.367354
C	-2.299882	4.546166	-0.462715
H	-1.635836	5.362955	-0.752428
H	-2.890948	4.901493	0.393507
H	-2.997173	4.404886	-1.294646
C	-2.399682	-0.300329	0.123079
C	-2.695694	-0.988179	-1.050848
C	-2.881028	-0.774083	1.339829
C	-3.657609	-1.924455	1.379659
C	-3.949358	-2.613157	0.209374
C	-3.464850	-2.141360	-1.005266
H	-4.554751	-3.513967	0.242266
H	-3.691553	-2.672864	-1.925125
H	-2.643449	-0.227296	2.248656
H	-4.036623	-2.283707	2.332149
H	-2.310515	-0.608202	-1.994154
Ti	0.517717	0.557254	0.176146
Cl	0.577450	-0.045909	2.462325
Cl	0.677843	0.686648	-2.205779
N	2.734332	0.125647	0.148888
C	3.274135	-1.030659	0.554219
C	4.636777	-1.262993	0.544974
C	5.482585	-0.256659	0.106406
C	4.931350	0.945996	-0.305809
C	3.557836	1.096351	-0.269375
H	3.086306	2.023223	-0.581954
H	6.557224	-0.407016	0.089735
H	5.551709	1.764642	-0.651723
H	2.584272	-1.793051	0.903658
H	5.020736	-2.218675	0.882455
C	0.552953	4.696334	0.250836
H	0.639338	5.168955	-0.734626
H	1.558987	4.539241	0.645232
H	0.022168	5.396448	0.904178
C	0.046502	-4.620052	-0.631761
C	-0.223750	-2.684671	0.734582
C	0.633570	-2.429046	-1.369581
C	-0.345329	-4.053402	0.569641
C	0.550289	-3.787692	-1.617962
N	0.250998	-1.865822	-0.214462
H	-0.036989	-5.689813	-0.795989
H	1.016434	-1.752117	-2.126914
H	-0.517508	-2.218054	1.668826
H	-0.745863	-4.655330	1.377828
H	0.877725	-4.177289	-2.575348

IM2

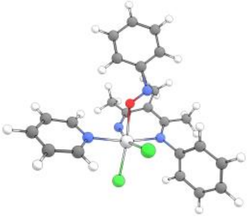
Electronic energy: -2593.136684
Gibbs free energy: -2592.866686
Corrected free energy: -2592.865142



42
IM2

C	-3.729814	1.277409	0.342714
C	-2.247137	1.344653	0.131807
H	-4.261139	1.467388	-0.598175
H	-4.052050	2.045569	1.049418
H	-4.051245	0.306413	0.719217
N	-1.539969	0.220844	0.065812
C	-1.670722	2.641786	0.003840
C	-0.307575	2.794914	-0.258239
N	0.487653	1.737304	-0.335595
C	-2.568008	3.845371	0.084663
H	-2.034301	4.763104	-0.164329
H	-2.985028	3.984816	1.090512
H	-3.418026	3.777108	-0.604531
C	-2.208592	-1.038316	0.046680
C	-2.874603	-1.457647	-1.104668
C	-2.141136	-1.884490	1.150181
C	-2.744543	-3.135713	1.102478
C	-3.410580	-3.549544	-0.041204
C	-3.473969	-2.705196	-1.144585
H	-3.878932	-4.528305	-0.076575
H	-3.990050	-3.024412	-2.045142
H	-1.631172	-1.548021	2.047962
H	-2.694830	-3.786868	1.970137
H	-2.903731	-0.796349	-1.966626
Ti	0.538894	0.050330	-0.008325
Cl	0.679105	-0.032875	2.326430
Cl	0.502969	-1.017662	-2.087970
N	2.728016	-0.368701	-0.013387
C	3.183474	-1.608884	0.202744
C	4.529539	-1.915434	0.204306
C	5.442859	-0.897176	-0.027303
C	4.975383	0.387730	-0.249664
C	3.610668	0.611912	-0.234353
H	3.193698	1.600389	-0.403387
H	6.507936	-1.104949	-0.034077
H	5.654172	1.212144	-0.434359
H	2.434046	-2.376927	0.378336
H	4.850655	-2.934869	0.383023
C	0.321992	4.139981	-0.476560
H	-0.123023	4.654084	-1.335280
H	1.391644	4.021813	-0.659508
H	0.187126	4.785475	0.397889

IM3
Electronic energy: -2954.535263
Gibbs free energy: -2954.175515
Corrected free energy: -2954.173311



55
IM3

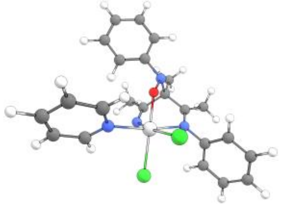
C	1.339341	-3.397954	0.826236
C	0.765386	-2.016510	0.925110
H	0.991123	-3.879014	-0.097824
H	1.013943	-4.020665	1.661332
H	2.428645	-3.390058	0.801289
N	1.447440	-0.967968	0.501635
C	-0.543881	-1.922502	1.515554
C	-1.000178	-0.694401	2.030423
N	-0.412208	0.413578	1.666983
C	-1.339913	-3.165597	1.765749
H	-2.410712	-2.938954	1.797731
H	-1.085509	-3.655929	2.716288
H	-1.198447	-3.905895	0.972545
C	2.754209	-1.190717	-0.038330
C	2.904863	-1.752547	-1.302970
C	3.873641	-0.812958	0.690654
C	5.142291	-1.002665	0.157690
C	5.295185	-1.565605	-1.100930
C	4.171763	-1.942013	-1.828718
H	6.287458	-1.707613	-1.518200
H	4.283888	-2.377531	-2.817206
H	3.742813	-0.368668	1.672808
H	6.014659	-0.704967	0.731752
H	2.016589	-2.022496	-1.868542
Ti	0.617439	0.994055	0.317874
Cl	2.217933	2.205917	1.447942
Cl	1.593234	1.187375	-1.882011
C	-2.196535	-0.627647	2.934702
H	-3.118806	-0.757370	2.351412
H	-2.234977	0.350371	3.419397
H	-2.184847	-1.406393	3.703439
H	-5.695738	-0.645444	-0.572628
H	-3.394079	0.299783	-0.426424
C	-4.833229	-1.263874	-0.800217
C	-3.561438	-0.732412	-0.716721
C	-5.014717	-2.594616	-1.176790
H	-6.018932	-3.002006	-1.240629
C	-2.464090	-1.548973	-1.007004
C	-3.922409	-3.401342	-1.471853
C	-2.642843	-2.881009	-1.382198
H	-4.071595	-4.434306	-1.768128
H	-1.763076	-3.480309	-1.601055
N	-1.122277	-1.132677	-0.904695
O	-0.982717	0.086537	-0.696531
C	-2.072651	5.154098	-0.446148
C	-0.117904	3.849392	-0.843090
C	-1.767811	2.996357	0.516236
C	-0.833582	5.013353	-1.050110
C	-2.547811	4.124921	0.351558
N	-0.572874	2.850403	-0.074281
H	-2.658901	6.055619	-0.592389
H	-2.087520	2.172560	1.148684
H	0.851431	3.695508	-1.307251
H	-0.418023	5.792055	-1.678905
H	-3.507817	4.192232	0.850183

TS1
Electronic energy: -2954.533841
Gibbs free energy: -2954.172410
Corrected free energy: -2954.170050

55
TS1

C	2.076118	-3.188499	0.529376
C	1.243275	-1.952610	0.668785
H	1.824560	-3.695770	-0.411120
H	1.875013	-3.890961	1.340571
H	3.142074	-2.965841	0.513471
N	1.715513	-0.770246	0.378588
C	-0.122853	-2.153042	1.145549
C	-0.786535	-1.101931	1.855359
N	-0.443612	0.116171	1.607513
C	-0.627994	-3.549197	1.297565
H	-1.721034	-3.568745	1.325206
H	-0.275945	-4.007268	2.232270
H	-0.308554	-4.193659	0.474512
C	3.059433	-0.672515	-0.103349
C	3.356817	-1.065898	-1.404110
C	4.052106	-0.150232	0.713787
C	5.347556	-0.029453	0.228088
C	5.649683	-0.422627	-1.067768
C	4.650193	-0.941934	-1.882647
H	6.662120	-0.319976	-1.446124
H	4.878430	-1.244835	-2.900077
H	3.802282	0.162821	1.722949
H	6.123123	0.379250	0.868759
H	2.558127	-1.450009	-2.034378
Ti	0.450798	0.990890	0.283577
Cl	1.734623	2.339755	1.668911
Cl	1.546056	1.685867	-1.751897
C	-1.937626	-1.410121	2.766735
H	-2.800329	-1.769836	2.190901
H	-2.233343	-0.503081	3.297271
H	-1.685916	-2.187053	3.496249
H	-5.375959	-0.554283	-0.371296
H	-2.993023	0.158248	-0.297821
C	-4.587751	-1.261763	-0.609922
C	-3.265971	-0.857455	-0.569085
C	-4.912516	-2.571569	-0.954724
H	-5.952828	-2.880085	-0.986638
C	-2.258711	-1.777020	-0.876892
C	-3.909929	-3.481069	-1.268884
C	-2.582720	-3.086521	-1.232281
H	-4.165196	-4.497705	-1.550345
H	-1.780001	-3.770817	-1.490664
N	-0.877757	-1.455098	-0.861914
O	-0.682697	-0.198497	-0.792693
C	-3.210972	4.332224	-0.331657
C	-1.510035	2.939467	-1.252267
C	-1.747827	3.043144	1.036871
C	-2.557116	3.822121	-1.441373
C	-2.796195	3.936196	0.930818
N	-1.108698	2.551113	-0.034529
H	-4.033729	5.030319	-0.448024
H	-1.402670	2.694978	2.005546
H	-0.963605	2.523766	-2.093273
H	-2.845299	4.102683	-2.447712
H	-3.276522	4.308942	1.827933

IM4
Electronic energy: -2954.555506
Gibbs free energy: -2954.191685
Corrected free energy: -2954.189373



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IM4

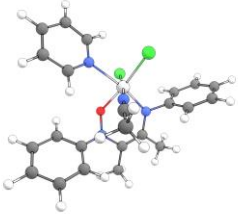
C	2.156069	-3.159082	0.270268
C	1.312979	-1.933260	0.330862
H	1.827649	-3.787363	-0.566156
H	2.038445	-3.754597	1.179258
H	3.211336	-2.928889	0.135791
N	1.775843	-0.751180	0.125126
C	-0.171071	-2.103646	0.655650
C	-0.588692	-1.159721	1.804213
N	-0.300151	0.056340	1.662654
C	-0.548886	-3.549699	0.904554
H	-1.613530	-3.648923	1.117591
H	-0.005572	-3.935965	1.770363
H	-0.319793	-4.180375	0.042203
C	3.167748	-0.576945	-0.165113
C	3.637637	-0.769732	-1.457995
C	4.034039	-0.206275	0.853735
C	5.383046	-0.035824	0.575234
C	5.861394	-0.226792	-0.713672
C	4.985892	-0.593102	-1.728225
H	6.916057	-0.086361	-0.929364
H	5.353633	-0.741007	-2.738989
H	3.644733	-0.051943	1.855454
H	6.061696	0.251623	1.372425
H	2.939541	-1.050131	-2.241474
Ti	0.372969	0.946698	0.112901
Cl	1.729736	2.296243	1.487494
Cl	1.391300	1.696553	-1.914085
C	-1.473984	-1.669054	2.899690
H	-2.423635	-2.040847	2.496796
H	-1.684595	-0.852773	3.593174
H	-1.008390	-2.494658	3.448647
H	-4.498560	-4.211595	-1.737692
H	-2.071155	-3.727684	-1.595220
C	-4.157350	-3.286733	-1.282781
C	-2.797515	-3.025473	-1.197999
C	-5.077821	-2.359773	-0.812552
H	-6.141923	-2.559996	-0.891018
C	-2.351511	-1.843204	-0.616666
C	-4.631314	-1.166679	-0.257903
C	-3.273498	-0.904246	-0.158206
H	-5.346223	-0.432316	0.101218
H	-2.919259	0.029154	0.268888
N	-0.934885	-1.592817	-0.565785
O	-0.705326	-0.267566	-0.774731
C	-3.351577	4.220453	-0.150556
C	-1.814076	2.727566	-1.191462
C	-1.654884	3.089124	1.081428
C	-2.889404	3.588896	-1.294365
C	-2.721799	3.966001	1.058029
N	-1.204479	2.478077	-0.023911
H	-4.192936	4.904114	-0.200061
H	-1.138115	2.855364	2.007223
H	-1.419068	2.214808	-2.063104
H	-3.349563	3.758129	-2.260745
H	-3.047937	4.438121	1.977283

TS2
Electronic energy: -2954.532551
Gibbs free energy: -2954.170506
Corrected free energy: -2954.169291

55
TS2

C	2.173904	-3.196770	-0.120444
C	1.234979	-2.028614	-0.228131
H	2.298074	-3.528674	0.918261
H	3.163623	-2.937269	-0.497047
H	1.807532	-4.050067	-0.696521
N	1.710737	-0.785681	-0.348380
C	-0.157979	-2.297446	-0.077345
C	-0.278503	-1.275866	1.754629
N	-0.006689	-0.132157	1.548545
C	-0.584264	-3.726358	0.094776
H	-1.603190	-3.801393	0.476063
H	0.065930	-4.239879	0.804472
H	-0.545161	-4.277705	-0.853284
C	3.119139	-0.578156	-0.212049
C	3.872739	-0.198053	-1.314887
C	3.726348	-0.714315	1.033727
C	5.082386	-0.471544	1.172198
C	5.839424	-0.090873	0.069778
C	5.232665	0.041901	-1.171050
H	6.901336	0.106181	0.180889
H	5.818555	0.340482	-2.035067
H	3.118230	-0.990244	1.891990
H	5.550892	-0.570467	2.146840
H	3.383795	-0.085919	-2.277320
Ti	0.540676	0.874750	-0.168136
Cl	1.931441	2.224805	1.155633
Cl	1.185035	1.857772	-2.210133
C	-0.911315	-2.191738	2.713725
H	-1.907648	-2.481390	2.364706
H	-1.014643	-1.677006	3.673105
H	-0.319267	-3.099702	2.853567
H	-5.108729	-3.622119	-1.484912
H	-2.662041	-3.395229	-1.741936
C	-4.592530	-2.795228	-1.006960
C	-3.217278	-2.679839	-1.144105
C	-5.309867	-1.845639	-0.291305
H	-6.387939	-1.931853	-0.198866
C	-2.545386	-1.623083	-0.534854
C	-4.641466	-0.775077	0.288969
C	-3.265135	-0.660155	0.171752
H	-5.194124	-0.019899	0.840509
H	-2.741811	0.177391	0.621594
N	-1.135067	-1.474754	-0.714147
O	-0.799091	-0.184717	-0.870901
C	-3.414050	3.899615	0.438060
C	-1.930021	2.654800	-0.949688
C	-1.444133	2.863484	1.290164
C	-3.080342	3.409622	-0.814451
C	-2.577690	3.623630	1.508895
N	-1.123729	2.377444	0.083452
H	-4.312682	4.491843	0.577992
H	-0.766339	2.621000	2.103226
H	-1.640579	2.246612	-1.913239
H	-3.698967	3.604541	-1.682729
H	-2.793603	3.990447	2.505676

IM5
Electronic energy: -2954.565283
Gibbs free energy: -2954.208628
Corrected free energy: -2954.205857



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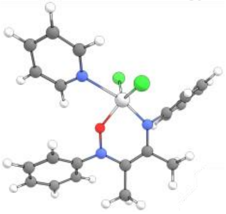
IM5

C	2.260007	-3.113549	-1.160543
C	1.187651	-2.105686	-0.867146
H	1.862737	-4.007143	-1.639857
H	2.779898	-3.433955	-0.250610
H	3.021797	-2.689266	-1.824831
N	1.597687	-0.841052	-0.445640
C	-0.125889	-2.424611	-1.072436
C	-0.724917	-0.527673	2.497509
N	-0.296743	0.001560	1.572626
C	-0.554411	-3.758146	-1.621268
H	-0.338421	-4.588559	-0.940325
H	-0.044612	-3.967158	-2.567539
H	-1.624771	-3.772687	-1.830161
C	2.944843	-0.729422	0.022390
C	3.918587	-0.129206	-0.767022
C	3.274969	-1.196768	1.292985
C	4.564831	-1.049001	1.774315
C	5.535899	-0.435958	0.989746
C	5.210256	0.018031	-0.280335
H	6.545109	-0.312594	1.370787
H	5.964936	0.495939	-0.897805
H	2.501915	-1.662745	1.899890
H	4.814720	-1.405963	2.769174
H	3.648547	0.233281	-1.754582
Ti	0.559670	0.784704	-0.313631
Cl	1.857067	2.094141	1.176315
Cl	1.297967	1.877816	-2.255331
C	-1.269095	-1.188922	3.651249
H	-0.785349	-2.159736	3.784380
H	-2.343469	-1.340228	3.516913
H	-1.098941	-0.580403	4.542596
H	-4.262736	-3.862131	1.430506
H	-1.938573	-3.426788	0.733710
C	-4.052855	-3.037276	0.755605
C	-2.744949	-2.803455	0.357804
C	-5.084376	-2.216173	0.318712
H	-6.104818	-2.399145	0.639601
C	-2.458165	-1.747780	-0.512876
C	-4.794200	-1.156206	-0.533496
C	-3.496354	-0.921696	-0.955069
H	-5.591763	-0.509144	-0.887398
H	-3.270173	-0.103981	-1.631044
N	-1.143681	-1.489957	-0.917940
O	-0.839565	-0.179752	-1.045008
C	-3.003807	4.386158	0.189372
C	-0.769899	3.717368	-0.308681
C	-2.299050	2.112999	0.281337
C	-1.712040	4.721806	-0.183749
C	-3.301654	3.054023	0.427593
N	-1.051674	2.427232	-0.084306
H	-3.765962	5.151833	0.293932
H	-2.498947	1.061153	0.455281
H	0.249990	3.946185	-0.601309
H	-1.428272	5.749303	-0.380097
H	-4.296050	2.737543	0.722891

IM6
Electronic energy: -2821.841276
Gibbs free energy: -2821.526602
Corrected free energy: -2821.524094



49
IM6

C	2.280261	-3.055308	1.103448
C	1.191540	-2.111296	0.693888
H	2.848536	-3.424021	0.241140
H	1.893163	-3.926966	1.630624
H	2.996191	-2.553342	1.764526
N	1.584554	-0.826163	0.310766
C	-0.122363	-2.469422	0.750694
N	-1.141810	-1.579057	0.432784
O	-0.889545	-0.252590	0.448962
C	-0.566988	-3.808774	1.265371
H	-1.639566	-3.823473	1.461682
H	-0.068487	-4.034457	2.212164
H	-0.342410	-4.625960	0.571252
C	2.915855	-0.642228	-0.167870
C	3.291879	-1.197281	-1.394025
C	3.821702	0.140654	0.541216
C	5.088848	0.379310	0.019837
C	5.458043	-0.169228	-1.197197
C	4.556524	-0.965279	-1.900221
H	6.446900	0.019636	-1.603445
H	4.841500	-1.395365	-2.855710
H	3.532870	0.550573	1.504232
H	5.789252	0.994848	0.575988
H	2.567733	-1.791158	-1.946157
Ti	0.578946	0.786811	0.234931
Cl	1.093355	1.563788	-1.876999
Cl	1.138325	1.745298	2.273514
H	-5.614779	-0.717831	0.337296
H	-3.304956	-0.214524	1.062791
C	-4.798805	-1.358835	0.016939
C	-3.508376	-1.069726	0.427054
C	-5.055576	-2.466514	-0.782674
H	-6.069882	-2.692430	-1.095640
C	-2.451892	-1.889950	0.024957
C	-4.002055	-3.276707	-1.184372
C	-2.702011	-2.987526	-0.798829
H	-4.187911	-4.134165	-1.824083
H	-1.877304	-3.600537	-1.148128
H	-4.034156	2.776311	-1.471969
H	-2.242284	1.127165	-1.035539
C	-3.170586	3.060410	-0.881374
C	-2.173273	2.135409	-0.638346
C	-3.033569	4.339761	-0.364881
H	-3.796764	5.091464	-0.538696
N	-1.083215	2.413808	0.087914
C	-1.900821	4.641031	0.372504
C	-0.953624	3.652717	0.575564
H	-1.744239	5.628039	0.792284
H	-0.057401	3.855196	1.154084

TS3

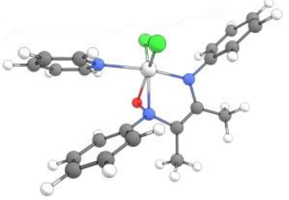
Electronic energy: -2821.840769
Gibbs free energy: -2821.524205
Corrected free energy: -2821.522527

49
TS3

C	-3.271976	1.386677	-1.849760
C	-1.893597	1.182313	-1.308455
H	-3.617110	0.490511	-2.378162
H	-3.304778	2.221593	-2.550612
H	-3.996560	1.585146	-1.051938
N	-1.647600	0.040696	-0.539025
C	-0.881267	2.038105	-1.585446
N	0.420119	1.721905	-1.156930
O	0.811640	0.404628	-1.330519
C	-1.004850	3.296385	-2.389217
H	-0.123535	3.926522	-2.244774
H	-1.883428	3.884555	-2.107906
H	-1.073628	3.084357	-3.464174
C	-2.781330	-0.504879	0.148178
C	-3.477475	-1.594839	-0.363527
C	-3.199649	0.088662	1.337725
C	-4.309235	-0.404478	2.006117
C	-5.003285	-1.494971	1.495433
C	-4.586192	-2.086571	0.310942
H	-5.869518	-1.883424	2.022281
H	-5.127358	-2.936403	-0.093858
H	-2.644682	0.940676	1.723560
H	-4.632247	0.062893	2.931479
H	-3.146744	-2.047152	-1.293437
Ti	0.050992	-0.796320	-0.184224
Cl	-0.413870	-2.916816	-0.867679
Cl	0.195206	-0.418038	2.044949
H	0.682089	4.936485	2.066083
H	-0.560072	3.674696	0.354647
C	1.186783	4.148862	1.514207
C	0.484727	3.448389	0.545198
C	2.508952	3.837549	1.798759
H	3.048540	4.381895	2.567003
C	1.117131	2.426864	-0.168959
C	3.129986	2.813007	1.094081
C	2.450118	2.113450	0.112374
H	4.162964	2.554936	1.308539
H	2.939526	1.316641	-0.436302
H	4.871251	-1.861204	-2.171138
H	2.608678	-0.857620	-2.009118
C	4.275606	-2.010502	-1.277994
C	3.013717	-1.452032	-1.195041
C	4.748022	-2.753475	-0.207704
H	5.734859	-3.203764	-0.239783
N	2.226409	-1.596025	-0.121337
C	3.935426	-2.912861	0.903231
C	2.685104	-2.323020	0.904761
H	4.258593	-3.486586	1.764091
H	2.022703	-2.432060	1.758632

IM7

Electronic energy: -2821.863095
Gibbs free energy: -2821.546380
Corrected free energy: -2821.544636



49
IM7

C	-2.893235	2.637880	-1.038915
C	-1.696357	1.802990	-0.733060
H	-3.510979	2.158171	-1.806543
H	-2.615474	3.631204	-1.391750
H	-3.524308	2.759438	-0.152417
N	-1.874743	0.481477	-0.353940
C	-0.418954	2.240287	-0.862059
N	0.547945	1.212996	-0.569639
O	0.591290	0.234650	-1.590853
C	0.096800	3.510674	-1.436813
H	0.694104	4.086554	-0.719182
H	-0.714684	4.154303	-1.779317
H	0.743574	3.305678	-2.301151
C	-3.167155	0.066204	0.077936
C	-3.990801	-0.660719	-0.776894
C	-3.615074	0.387392	1.357765
C	-4.876584	-0.011885	1.773517
C	-5.697364	-0.736280	0.918562
C	-5.251658	-1.058189	-0.356777
H	-6.683280	-1.051181	1.246881
H	-5.889602	-1.622376	-1.030540
H	-2.962023	0.950824	2.018810
H	-5.218799	0.241747	2.772500
H	-3.631893	-0.906187	-1.772334
Ti	-0.286588	-0.658950	-0.218842
Cl	-1.129670	-2.568699	-1.122885
Cl	-0.352750	-0.663286	2.102048
H	3.219429	3.039271	2.637788
H	1.006565	2.374547	1.722601
C	3.156538	2.568729	1.661679
C	1.918511	2.203881	1.156772
C	4.311929	2.322207	0.929380
H	5.280420	2.601592	1.332068
C	1.846465	1.594979	-0.090125
C	4.224312	1.718947	-0.317885
C	2.989662	1.354559	-0.837328
H	5.123682	1.529288	-0.895848
H	2.905228	0.876083	-1.806736
H	3.963205	-3.127856	-2.075566
H	1.699841	-2.158576	-1.976671
C	3.594584	-2.716022	-1.143287
C	2.323557	-2.179410	-1.088119
C	4.371757	-2.710550	0.005410
H	5.377403	-3.118414	-0.005343
N	1.798584	-1.657062	0.030604
C	3.838181	-2.175899	1.165237
C	2.552236	-1.665289	1.136822
H	4.403925	-2.148074	2.089268
H	2.102807	-1.241367	2.028966

TS4

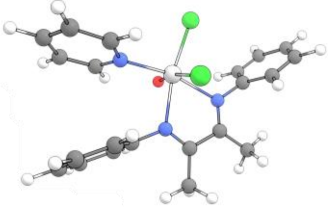
Electronic energy: -2821.855518
Gibbs free energy: -2821.540278
Corrected free energy: -2821.538276

49
TS4

C	-2.745903	2.935123	-0.600063
C	-1.592454	2.000229	-0.455228
H	-3.514003	2.717941	0.146931
H	-3.216164	2.831086	-1.584905
H	-2.436573	3.973590	-0.479109
N	-1.780331	0.691603	-0.187161
C	-0.277578	2.430529	-0.590859
N	0.632415	1.442025	-0.307346
O	0.753631	0.324490	-1.494101
C	0.190363	3.741638	-1.129227
H	0.796587	4.301210	-0.406194
H	-0.645927	4.376331	-1.425309
H	0.809941	3.590674	-2.022328
C	-3.097464	0.220416	0.082057
C	-3.991844	-0.003001	-0.961559
C	-3.479238	-0.055096	1.390414
C	-4.753245	-0.543033	1.651919
C	-5.646967	-0.759864	0.612953
C	-5.261887	-0.488409	-0.694737
H	-6.640884	-1.144945	0.819531
H	-5.953763	-0.662835	-1.513435
H	-2.769157	0.112906	2.195146
H	-5.045896	-0.755900	2.675852
H	-3.672476	0.191828	-1.981995
Ti	-0.136742	-0.517702	-0.216371
Cl	-1.391958	-2.203868	-1.142519
Cl	0.061704	-0.635438	2.113827
H	3.590395	2.858396	2.837054
H	1.335029	2.134037	2.087161
C	3.430465	2.572781	1.802202
C	2.168413	2.170446	1.392165
C	4.484835	2.598324	0.898841
H	5.473214	2.906298	1.225356
C	1.967713	1.801508	0.066930
C	4.272730	2.228506	-0.422604
C	3.011879	1.835955	-0.847772
H	5.092744	2.253486	-1.133645
H	2.829105	1.554115	-1.878774
H	4.558113	-2.560567	-1.636259
H	2.679859	-0.941787	-1.550021
C	3.701033	-2.759501	-1.003286
C	2.659761	-1.849839	-0.956954
C	3.617889	-3.909716	-0.237361
H	4.416359	-4.644598	-0.253758
N	1.575412	-2.028535	-0.192224
C	2.493269	-4.106112	0.549873
C	1.501985	-3.145255	0.546473
H	2.379221	-4.991598	1.164165
H	0.612886	-3.267376	1.157338

IM8

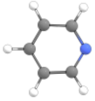
Electronic energy: -2821.930796
Gibbs free energy: -2821.614194
Corrected free energy: -2821.613251



49
IM8

C	-2.692679	3.072158	0.216472
C	-1.673170	2.008853	0.043741
H	-2.434092	3.953967	-0.376106
H	-2.721963	3.388317	1.266687
H	-3.687687	2.728481	-0.066114
N	-1.918935	0.767351	-0.145765
C	-0.220486	2.373685	0.091680
N	0.589220	1.389195	0.003449
C	0.164374	3.799733	0.237800
H	1.231575	3.912924	0.428264
H	-0.394594	4.259039	1.059127
H	-0.088992	4.355599	-0.672841
C	-3.252210	0.267383	-0.182301
C	-3.766427	-0.175500	-1.394657
C	-3.986433	0.151905	0.991346
C	-5.254512	-0.407750	0.943743
C	-5.784695	-0.839526	-0.264745
C	-5.041182	-0.718372	-1.431866
H	-6.776746	-1.278910	-0.296273
H	-5.449970	-1.061630	-2.376995
H	-3.547401	0.477022	1.930274
H	-5.828588	-0.510646	1.859261
H	-3.156406	-0.102675	-2.290314
Ti	-0.245657	-0.664226	-0.326952
Cl	-1.424227	-2.671700	-0.246773
Cl	-0.338706	-0.466561	2.307367
H	4.755502	1.288619	1.881246
H	2.281902	1.014541	1.997328
C	4.147264	1.481352	1.002769
C	2.770094	1.332630	1.080233
C	4.747055	1.870984	-0.188726
H	5.825377	1.982531	-0.243518
C	1.995917	1.590488	-0.044905
C	3.964866	2.114201	-1.310159
C	2.585934	1.974260	-1.243764
H	4.428769	2.415109	-2.244495
H	1.957450	2.142472	-2.114126
H	4.451978	-2.082850	-2.041349
H	2.191271	-1.044408	-2.054279
C	3.825230	-2.135280	-1.158676
C	2.573598	-1.551178	-1.174332
C	4.248006	-2.779129	-0.006354
H	5.226238	-3.247172	0.037018
N	1.752542	-1.574444	-0.111905
C	3.397253	-2.821823	1.086885
C	2.161621	-2.210266	0.997408
H	3.679712	-3.322900	2.005418
H	1.466389	-2.206269	1.831906
O	-0.056465	-0.445663	-1.915910

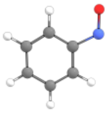
pyridine
Electronic energy: -248.159196
Gibbs free energy: -248.098400
Corrected free energy: -248.098400



11
py

C	0.718138	1.137600	-0.000000
C	-0.668412	1.192430	0.000000
C	-1.375862	0.000000	0.000000
C	-0.668412	-1.192430	0.000000
C	0.718138	-1.137600	-0.000000
N	1.410788	-0.000000	-0.000000
H	1.299888	-2.058260	-0.000000
H	-1.177562	-2.150450	0.000000
H	-2.461712	0.000000	0.000000
H	1.299888	2.058260	-0.000000
H	-1.177552	2.150450	0.000000

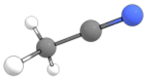
PhNO
Electronic energy: -361.381435
Gibbs free energy: -361.314959
Corrected free energy: -361.314959



13
PhNO

C	0.550971	-0.219292	-0.000020
C	-0.333310	-1.292700	-0.000010
C	-1.697780	-1.052119	0.000010
C	-2.159348	0.257752	0.000020
C	-1.267677	1.331301	-0.000010
C	0.092483	1.097859	-0.000030
H	-1.647025	2.348151	-0.000010
H	0.815324	1.907118	-0.000030
H	0.076198	-2.298761	-0.000020
H	-2.400101	-1.878988	0.000040
H	-3.227918	0.450544	0.000050
N	1.935581	-0.576234	-0.000030
O	2.715302	0.346095	0.000050

MeCN
Electronic energy: -132.699549
Gibbs free energy: -132.678363
Corrected free energy: -132.678363



6
MeCN

N	1.426808	-0.000010	0.000006
C	0.275288	0.000010	-0.000013
C	-1.167782	-0.000000	-0.000021
H	-1.544191	-0.116926	1.018956
H	-1.544313	-0.824031	-0.610646
H	-1.544192	0.940967	-0.408143

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